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Rationalization of lattice energy calculations,

- with particular reference to complex salts.

by

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A thesis submitted to the University of Warwick  
in partial fulfilment of the requirements for  
the degree of Doctor of Philosophy.

ACCEPTED

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August, 1978

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I wish to gratefully acknowledge the support, guidance and friendship shown to me by my supervisor, Dr. H.D.J. Jenkins, over the duration of this research. My gratitude also to all the staff of the Computer Unit at the University of Warwick, in particular Mr. J.D. Sheridan and Mr. M.S. Hunt, for their kind help with both my research and the production of this document (produced using the computer package 'Formatter', written by I.J. Lawrence and published by the Canberra College of Advanced Education, Australia (1977); as implemented on the Burroughs 6700 computer at the University of Warwick).

The Science Research Council is acknowledged for the provision of a postgraduate studentship award.

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The Science Research Council is acknowledged for the provision of a postgraduate studentship award.



**Declaration**

The material contained in this thesis is the authors original work which has not been submitted in part or in whole for consideration towards any other degree of this or any other university.

Parts of the work covered by this thesis have been published or accepted for publication in the scientific literature with the following references:

H.D.B. Jenkins and K.F. Pratt, *J. Inorg. Nucl. Chem.*,  
**38**, 1775 (1976)

H.D.B. Jenkins, K.F. Pratt and T.C. Waddington, *J.*  
*Inorg. Nucl. Chem.*, **39**, 217 (1977)

H.D.B. Jenkins and K.F. Pratt, *Proc. Roy. Soc.*,  
**A356**, 115 (1977)

H.D.B. Jenkins and K.F. Pratt, *J. Chem. Res.*, **64**  
(1977)

H.D.B. Jenkins and K.F. Pratt, *J. Phys. Chem. Solids*,  
**38**, 573 (1977)

H.D.B. Jenkins and K.F. Pratt, *J.C.S. Faraday II*, **812**  
(1977)

H.D.B. Jenkins and K.F. Pratt, *Comp. Phys. Comm.*,  
**13**, 341 (1978)

H.D.B. Jenkins and K.F. Pratt, *J.C.S. Faraday II*,  
**74**, 968 (1978)

H.D.B. Jenkins and K.F. Pratt, *Adv. Inorg. Chem.*  
*Radiochem.*, **22**, at the printers (1978)

H.D.B. Jenkins and K.F. Pratt, *Prog. Solid State*  
*Chem.*, accepted for publication (1978)

Reprints of the available papers are included in  
Appendix A at the end of this report.

To my mother

## Summary

A method is presented for the general calculation of lattice energies for complex salts. It involves the minimisation of the energy of the salt with respect to the cell lengths of the experimental crystal structure. The Bertaut method is differentiated for the calculation of the electrostatic energy contribution. A Huggins and Mayer form for the repulsion energy and a London form for the dispersion energy are used, after consideration of the alternatives. An investigation of the dependence of the results obtained from the method on the various input parameters is presented. Basic radii for many monatomic ions are computed for use in the calculations.

The method is completely implemented in a computer program designed to be used by chemists unfamiliar with the underlying theory.

Calculations are reported for salts of the cyanide, azide, bifluoride, hexahalometallate(IV) (118 salts), perchlorate, tetrachloroaluminate, peroxide and hexafluorotungstate(V) ions. Lattice energies are combined with experimental data in thermochemical cycles to predict much thermodynamic data for these ions. The results encourage the belief that the method is generally applicable.

## C O N T E N T S

1. Introduction	1
1.1 General	1
1.2 The Definition of Lattice Energy	3
1.3 Lattice Energy in Thermochemistry	4
1.4 True versus Calculated Lattice Energy	9
1.5 Empirical and Non-empirical Calculation	14
1.6 Lattice Energies from other Methods	19
1.7 Aims of the Research	24
2. Theory	27
2.1 Term-by-Term Approach	27
2.2 Electrostatic Energy	29
2.3 Repulsion Energy	44
2.4 Dispersion Energy	51
2.5 Energy Minimisation	61
2.6 Compressibility of a Solid	71
2.7 New General Method	74
2.8 Parameter Dependence	84
3. Computer Programs	100
3.1 Introduction	100
3.2 LATEN - Lattice Energy Program	101
3.3 Graph Plotting	121

3.4 Bond Lengths and Bond Angles	123
3.5 Atomic Coordinate Computation	124
3.6 Multipole Moment Expansion	124
4. Results	126
4.1 Introduction	126
4.2 Evaluation of Basic Radii	129
4.3 The Cyanide Ion	137
4.4 The Azide Ion	154
4.5 The Difluoride Ion	167
4.6 Hexahalometallate(IV) Ions	176
4.7 The Perchlorate Ion	193
4.8 The Tetrachloroaluminate Ion	193
4.9 The Peroxide Ion	200
4.10 The Hexafluorotungstate(V) Ion	205
5. Conclusions	212
6. References	218
INDEX	234

### List of Figures

Figure	Page	Title
1.3(i)	7	'Level' form for the thermochemical cycle.
1.3(ii)	7	'Tetrahedron' form for the thermochemical cycle.
1.4(i)	10	Comparison of true and calculated lattice energies.
2.4(i)	60	Convergence of the dispersion energy summations.
2.8(i)	85	Lattice energy of potassium hexafluorogermanate.
2.8(ii)	92	Example of lattice energy dependence on dipole-dipole dispersion energy.
2.8(iii)	92	Example of lattice energy dependence on dipole-quadrupole dispersion energy.
2.8(iv)	93	Example of lattice energy dependence on ion polarisability.
2.8(v)	93	Example of lattice energy dependence on ion characteristic energy.
2.8(vi)	94	Example of lattice energy dependence on ion electron number.
2.8(vii)	95	Example of lattice energy dependence on ion basic radius.
2.8(viii)	96	Example of lattice energy dependence on repulsion exponent.

2.8(ix)	98	Repulsion envelopes for hexafluorogermanate(IV) ion.
2.8(x)	99	Complete curves for the lattice energy of potassium hexafluorogermanate.
3.2(i)	114	Convergence of electrostatic energy using a uniform charge density function.
3.2(ii)	114	Convergence of electrostatic energy using a linear charge density function.
3.2(iii)	114	Convergence of electrostatic energy using a parabolic charge density function.
3.2(iv)	114	Convergence of electrostatic energy using a Gaussian charge density function.
4.3(i)	143	Lattice energy of sodium cyanide(II) for the one and two sphere repulsion models.
4.3(ii)	146	Lattice energy of the polymorphs of sodium cyanide for the ellipsoidal repulsion model.
4.3(iii)	146	Lattice energy of the polymorphs of potassium cyanide for the ellipsoidal repulsion model.
4.3(iv)	147	Lattice energy of ammonium cyanide for the ellipsoidal repulsion model.
4.3(v)	148	Enthalpy of formation of the gaseous cyanide ion.
4.4(i)	159	Lattice energy of lithium azide.
4.4(ii)	160	Lattice energy of the polymorphs of sodium azide.



4.4(iii)	160	Lattice energy of potassium azide.
4.4(iv)	160	Lattice energy of ammonium azide.
4.4(v)	160	Lattice energy of silver azide.
4.4(vi)	160	Lattice energy of copper(I) azide.
4.4(vii)	166	Enthalpy of formation of the gaseous azide ion.
4.5(i)	171	Lattice energy of lithium bifluoride.
4.5(ii)	171	Lattice energy of potassium bifluoride.
4.5(iii)	171	Lattice energy of ammonium bifluoride.
4.5(iv)	173	Enthalpy of formation of the gaseous bifluoride ion.
4.5(v)	174	Thermochemical cycle giving the hydrogen bond strength of the bifluoride ion.
4.5(vi)	174	Hydrogen bond strength of the bifluoride ion.
4.6(i)	192	Lattice energy of potassium hexachloroplatinate(IV) for two repulsion models.
4.8(i)	196	Lattice energy of lithium tetrachloroaluminate.
4.8(ii)	196	Lattice energy of sodium tetrachloroaluminate.
4.8(iii)	196	Lattice energy of potassium tetrachloroaluminate.
4.8(iv)	196	Lattice energy of cesium tetrachloroaluminate.
4.8(v)	198	Enthalpy of formation of the gaseous

tetrachloroaluminate ion.

4.8(vi) 179 Basic radius of the chlorine atoms of the  
tetrachloroaluminate ion.

4.9(i) 204 Enthalpy of formation of the gaseous  
peroxide ion.

4.10(i) 206 Lattice energy of lithium  
hexafluorotungstate(V).

4.10(ii) 207 Lattice energy of sodium  
hexafluorotungstate(V).

4.10(iii) 207 Lattice energy of potassium  
hexafluorotungstate(V).

4.10(iv) 207 Lattice energy of cesium  
hexafluorotungstate(V).

4.10(v) 209 Enthalpy of formation of the gaseous  
hexafluorotungstate(V) ion.

### List of Tables

Table	Page	Title
2.7(i)	81	Amplification of the general terms of Equation 2.7(iv).
2.8(i)	89	Dispersion energy, and cell length derivatives, for potassium hexafluorogermanate.
2.8(ii)	97	Results for the various repulsion models of the hexafluorogermanate ion.
3.2(i)	121	Sample data input for LATEN, using the full facilities of the program.
4.2(i)	133	Coefficients, for the calculation of the dispersion energy for salts composed of simple monatomic ions.
4.2(ii)	133	Coefficients of Equation 4.2(vi) for cubic salts.
4.2(iii)	134	Basic radii obtained by the least squares fit.
4.2(iv)	135	Finally assigned basic radii for ions.
4.2(v)	136	Ammonium halide results giving the basic radius of the ammonium ion.
4.3(i)	141	Details of the unit cells of cyanide salts.
4.3(ii)	146	Anion-cation and anion-anion contacts in some cyanide crystals.

4.3(iii)	148	Intermediate results for cyanide salts not treated in Jenkins and Pratt (1975).
4.3(iv)	148	Thermochemical data for cyanide salts.
4.4(i)	155	Details of the unit cells of azide salts.
4.4(ii)	157	Intermediate results for lithium, sodium, potassium and rubidium azide salts.
4.4(iii)	157	Intermediate results for cesium, ammonium, thallium, silver and copper(I) azide salts.
4.4(iv)	160	Coordinates of the intersection points on Figures 4.4(i)-4.4(vi), using the three sphere model of the azide ion.
4.4(v)	161	Coordinates of the intersection points on Figures 4.4(i)-4.4(vi), using the two sphere model of the azide ion.
4.4(vi)	162	Lattice energies assigned for azide salts. Enthalpy of formation of the gaseous azide ion.
4.4(vii)	164	Thermochemical data for azide salts.
4.5(i)	169	Unit cell details for bifluoride salts.
4.5(ii)	169	Intermediate results for alkali metal bifluorides.
4.5(iii)	170	Intermediate results for ammonium bifluoride.
4.5(iv)	171	Coordinates of intersection points for bifluoride salts.
4.5(v)	173	Thermochemical data for bifluoride and

fluoride salts.

4.6(i)	178	Coefficients for the multipole moment expansion of the Madelung constant of the potassium hexachloroplatinate structure.
4.6(ii)	180	Unit cell details for hexahalometallate(IV) salts.
4.6(iii)	191	Electrostatic energy for non-cubic hexahalometallate(IV) salts.
4.6(iv)	181	Cell length derivatives of the electrostatic energy for non-cubic hexahalometallate(IV) salts.
4.6(v)	181	Dispersion energies for hexahalometallate(IV) salts.
4.6(vi)	185	Calculated lattice energies for hexahalometallate(IV) salts.
4.6(vii)	186	Lattice energies of further hexahalometallate(IV) salts estimated by Equations 4.6(viii)-4.6(xi).
4.6(viii)	186	Enthalpies of formation of gaseous hexahalometallate(IV) ions.
4.6(ix)	187	Thermochemical results and bond energies for hexahalometallate(IV) ions.
4.6(x)	191	Double halide ion affinities of metal tetrafluorides.
4.8(i)	195	Unit cell details for tetrachloroaluminate salts.
4.8(ii)	195	Intermediate results for

		tetrachloroaluminate salts.
4.8(iii)	197	Intersection points to be used for assignment of values for tetrachloroaluminate salts.
4.8(iv)	198	Ancillary thermochemical data for use in the tetrachloroaluminate ion calculations.
4.9(i)	201	Unit cell details for metal peroxides.
4.9(ii)	201	Intermediate results for alkali metal peroxides.
4.9(iii)	201	Intermediate results for alkaline earth metal peroxides.
4.9(iv)	202	Final results for metal peroxides.
4.9(v)	203	Thermochemical data for peroxide salts.
4.10(i)	206	Proposed unit cell details for hexafluorotungstate(V) salts.
4.10(ii)	206	Intermediate results for hexafluorotungstate(V) salts.
4.10(iii)	209	Thermochemical data for hexafluorotungstate(V) salts.

## **1. Introduction**

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### **1.1 General**

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The ability to estimate lattice energies for salts is an important asset in the study of inorganic energetics. It enables the complete solution of thermochemical cycles which contain steps impossible to investigate by experimental procedures.

The lattice energy step in a thermochemical cycle was formulated by Born and Haber in 1919. The first application of such a cycle was the investigation of the electron affinities of halogen atoms. In fact the major part of this century has been taken up with investigations of simple systems such as this, another example of which is the prediction of the stability of hypothetical compounds involving unusual oxidation states of elements. These studies have been performed with such success that further calculation along similar lines would seem to be of little purpose. Waddington (1959) has presented a review of such calculations.

The future of the use of lattice energies is the solution of thermochemical cycles involving complex, rather than monatomic, ions. The thermochemical data derived by such studies can be used by inorganic chemists for prediction of the energetics for compounds, both before and after preparation (if this is proved to be energetically favourable). Other useful quantities which it is possible to obtain are the stabilities (enthalpic) of complex ions with respect to neutral molecules; examples being the electron, proton and halide ion affinities of these molecules.

This report describes the development of a rigorous, computer based, method for the calculation of lattice energies for salts composed of complex ions, and its application to a variety of systems as an illustration of the results that can be obtained. Section 1 gives a brief account of the concept of lattice energy, its calculation and place within chemistry. Section 2 describes the chosen potential, its history of development and gives details of the approach proposed for the calculation of lattice energies. The third shows how computers can be used to generally apply the approach and the fourth gives examples of its use. The method is designed to be applied by all chemists as a tool in their research, with a view to the

## Introduction



integration of extended lattice energy calculations and practical studies on inorganic systems, Subjects which have generally previously been separated despite often seeking similar objectives.

## 1.2 The Definition of Lattice Energy

Since the introduction of the concept of 'lattice energy' around the beginning of this century different workers have used different working definitions. Alternatives have been to cite a potential energy or enthalpy, and to define the process as ionic crystal going to gaseous ions or vice versa. The definition used in this work is of the **potential energy** change, at absolute zero, for the process of one mole of crystal being converted to its constituent ions in the gas phase, at infinite separation. For a simple crystal MX the process is depicted by:



where the potential energy change, the **lattice energy**, is symbolised by  $U_m(MX)$  and is a **positive** number when, as in all the cases considered in this work, the crystal is stable with respect to decomposition into its constituent ions. Subsequently any reference to a 'lattice

energy' symbolises the potential energy change for the above process.

### 1.3 Lattice Energy in Thermochemistry

In order to include a lattice energy in an enthalpic thermochemical cycle it first must be converted into a **lattice enthalpy**, which is the enthalpy change for the process of crystal going to gaseous ions, as defined in the previous section.

A general crystal can be considered to be composed of ions  $(I_i)^{q_i}$  (where  $q_i$  is the charge carried by the ion  $I_i$ , which may be monitonic or complex), appearing  $a_i$  times in the formula unit. The internal energy of an ion  $I_i$  is given by  $n_i RT/2$  where  $n_i$  is the number of degrees of freedom the ion possesses,  $R$  is the gas constant and  $T$  the absolute temperature. This internal energy is related to an enthalpy, for a perfect gas, by the addition of an extra  $RT$  term. Consequently the total enthalpy of the separated gaseous ions obtained from our general formula unit is  $\sum_i a_i (n_i + 2) RT/2$ .

The enthalpy of the crystal is related to its internal energy by the addition of a term  $PV_{MX}$  (where  $V_{MX}$  is

the volume occupied by a mole of the crystal at pressure  $p$ ) which is generally less than  $10 \text{ J. mol}^{-1}$  (at atmospheric pressure) and so can be neglected in these considerations. The internal energy is the sum of the potential and kinetic energy of the lattice. The potential energy is simply the negative of the lattice energy defined in the previous section. The kinetic energy (sometimes called the acoustic energy) of a crystal may be obtained from a knowledge of specific heat, as a function of temperature, and of the zero point energy of the lattice. This zero point energy term is given by either the Einstein theory as  $3R\Theta_E$  or the Debye theory as  $9R\Theta_D/4$ , where  $\Theta_E$  and  $\Theta_D$  are the Einstein and Debye temperatures. When considering temperatures considerably greater than the Einstein or Debye temperatures both theories support the classical theory that the kinetic energy of a crystal is  $3RT$  per ion. In simple cases, such as the alkali halides, the information necessary to obtain the internal kinetic energy of the lattice using the more modern theories is well established, but for many more complex crystals this information is absent. This fact makes the choice of the simple classical theory inevitable in many cases. The temperatures considered (generally around  $298\text{K}$ ), being reasonably high, make the errors incurred by the choice of the classical treatment small. This has led to the simple

classical theory being adopted in all cases for this work, the error introduced generally being less than the uncertainties in the thermochemical data.

The combination of the above terms gives the relationship between lattice enthalpy,  $\Delta H_U^\circ$ , and lattice energy,  $U_{POT}$  for a crystal constituted as described above, as:

$$\Delta H_U^\circ = \sum_i a_i(n_i + 2)RT/2 - \sum_i a_i 3RT + U_{POT} \quad 1.3(i)$$

$$= \frac{RT}{2} \sum_i a_i(n_i - 4) + U_{POT} \quad 1.3(ii)$$

where the sum is over all types of ion in the lattice and  $n_i$ , the number of degrees of freedom of the ion  $i$ , is 3 for a monatomic ion, 5 for a linear polyatomic and 6 for a non-linear polyatomic.

The lattice enthalpy can be used in a general Born-Hajans-Haber cycle which involves all possible conversions between the states:

- (a) the elemental standard states;
- (b) the crystalline state;
- (c) the separated gaseous ions;

#### Introduction

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$$= \frac{RT}{2} \sum_i a_i(n_i - 4) + U_{POT} \quad 1.3(ii)$$

where the sum is over all types of ion in the lattice and  $n_i$ , the number of degrees of freedom of the ion  $I_i$ , is 3 for a monatomic ion, 5 for a linear polyatomic and 6 for a non-linear polyatomic.

The lattice enthalpy can be used in a general Born-Fajans-Haber cycle which involves all possible conversions between the states:

- (a) the elemental standard states;
- (b) the crystalline state;
- (c) the separated gaseous ions;

(c) the separated hydrated ions;

-all under standard conditions. This cycle is given in its more conventional 'level' form in Figure 1.3(i) where the order of states is as found in simple ionic cases (except for the bottom levels, crystal and hydrated ions, which are often reversed, the enthalpy of solution being either positive or negative), and in the more easily conceived form of a tetrahedron with the four states at the apices, in Figure 1.3(ii). In Figure 1.3(ii) solid interconnecting lines indicate enthalpy changes usually obtainable experimentally and dotted lines those which are not. In both figures the standard enthalpy changes are defined such that:  $\Delta H_f^\circ(\text{crystal})$  refers to the formation of the crystal from elements (standard state);  $\Delta H_{\text{soln}}^\circ(\text{crystal})$  refers to the solution of the crystal in water to infinite dilution;  $\Delta H_f^\circ(\text{ion})(g)$  refers to the formation of a gaseous ion from elements;  $\Delta H_f^\circ(\text{ion})(ac)$  refers to the formation of an aqueous ion from elements;  $\Delta H_{\text{hyd}}^\circ(\text{ion})(g)$  refers to the hydration of the gaseous ion. The sum over ions is over all the ions which are present in the crystal.

On inspection of the tetrahedron, and noting that each face forms a closed cycle, it can be seen that one face can be completely determined experimentally whilst

#### Introduction

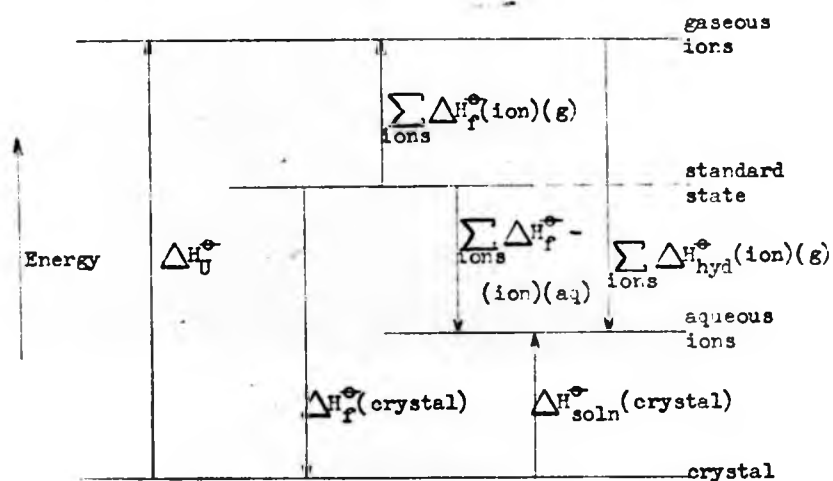


Figure 1.3(i) 'Level' form of thermochemical cycle.

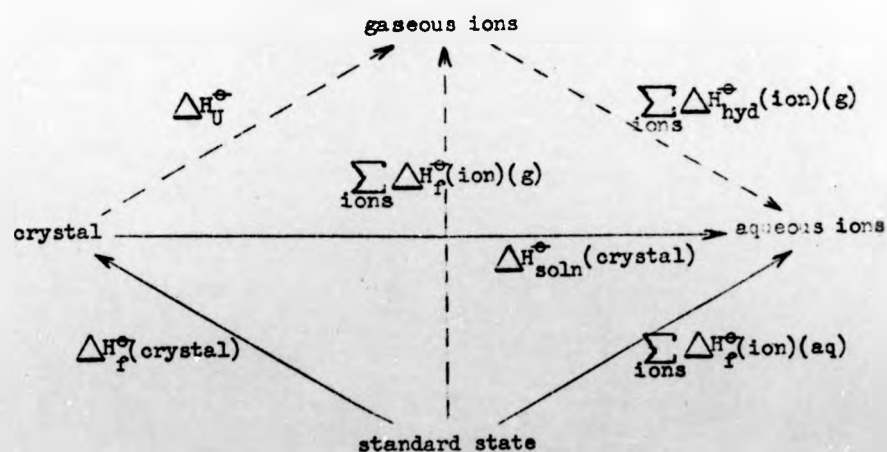


Figure 1.3(ii) 'Tetrahedron' form of thermochemical cycle.

the other three contain one 'known' and two 'unknown' enthalpy changes. It is evident that a determination of only one of the three 'unknown' enthalpy changes gives a complete solution for the cycle (from the observation that edges are shared by two 'triangular' cycles). The lattice enthalpy is one of these 'unknowns'.

It seems worthwhile to point out here that in many cases the so-called experimentally 'known' enthalpy changes are not always determined (in fact in some cases they are not even obtainable by present techniques). If only the enthalpy of formation **or** solution of the crystal is known a knowledge of the lattice enthalpy enables the solution of one, and only one, face of the tetrahedron; leaving the other three faces undetermined.

In a few simple cases (primarily the alkali halides) experimental values exist for the two 'unknown' tetrahedron edges (other than the lattice enthalpy) and so experimental (or Born-Haber) lattice enthalpies may be obtained to compare with calculated values.

Many extensions and refinements can be made to the basic cycle to include other thermochemical quantities, such as electron affinity. These sub-cycles will be



included in the sections where they are to be used.

#### **1.4 True versus Calculated Lattice Energy**

---

All current methods of calculating the lattice energy of a crystal assume a purely ionic model for that crystal. This means that the assumed decomposition of the crystal involves the breaking of no directional bonds between the constituent ions (note that this allows us to keep atoms directly bonded throughout the process which is essential for complex ions and neutral molecules). They also assume that the **atoms** of the crystal possess a spherically symmetrical electron cloud (recent work by Blake (1977) has gone some way to removing the necessity of this assumption). These restrictions mean that even if the method was perfect, i.e. it could calculate a **true ionic** lattice energy, the lattice enthalpy (see previous section) would not be completely determined for any real case. This arises because of the necessary departure of real crystals from the absolute ionic, spherical atom ideal.

The starting situation for the calculation of the lattice energy process is the ideal ionic crystal, this will be separated from the real crystal (a state defined

by its enthalpy of formation, see Figure 1.3(ii)) by an energy  $\Delta_1$ , see Figure 1.4(i). The energy  $\Delta_1$  comprises of terms which include:

- (a) any directional bonding (covalency, hydrogen-bonding) in the real crystal not present in the gaseous ions;
- (b) any departure from spherical electron density around atomic centres (obviously present in transition metal and complex ions);
- (c) at temperatures greater than absolute zero (considered by the lattice enthalpy but not the calculated lattice energy) a real crystal will have a degree of disorder, involving crystal defects.

The final state for the lattice energy process considered in this work is gaseous ions identical in geometry and charge distribution with those present in the crystal. For monatomic ions this is obviously equivalent to the 'true' state but for complex ions there will invariably be some change in geometry of the ion and redistribution of charge over the ion necessary to bring it to its equilibrium gaseous configuration, defined by its gaseous enthalpy of formation (Figure 1.3(ii)). In Figure 1.4(i) this energy is given as  $\Delta_2$ .

As can be seen in Figure 1.4(i) the effects of  $\Delta_1$  and

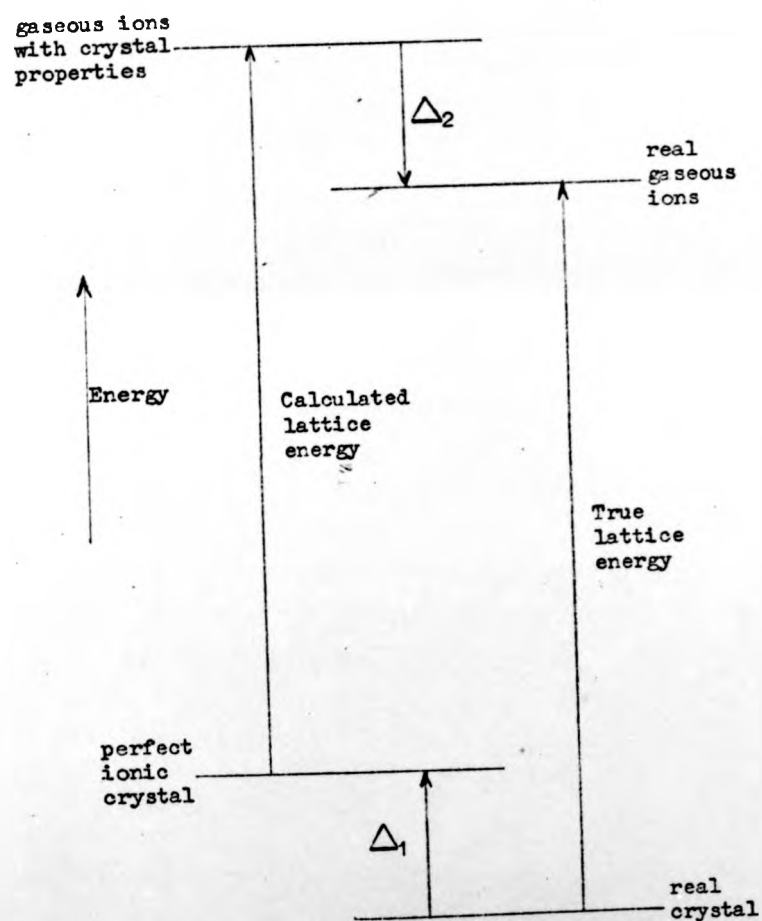


Figure 1.4 (i) Comparison of true and calculated lattice energies.

$\Delta_2$  on the lattice energy tend to cancel, however normally  $\Delta_2$  will be small (or zero when only monatomic ions are involved) and so there will inevitably be a finite difference between real and calculated lattice energies, of approximately  $\Delta_1$ . If  $\Delta_2$  is likely to be large, for complex ions greatly distorted in the solid state, it could be estimated by quantum mechanical calculations, though no such calculations have been performed or deemed necessary as yet.

Empirical estimates have been made (for example Pauling (1960) and Sanderson (1976)) concerning the (major) partial covalency contribution to  $\Delta_1$  in solids but these have not met with much success. The distortion of the spherical symmetry of the electron cloud around an atomic centre can be accommodated in electrostatic energy calculations by the introduction of multipole moment expansion techniques (for example Neckel, Vinek and Nowotny (1967); Redlack and Grindlay (1975); Blake (1977)) if the distortion is well understood, as for example in transition metal ions. But difficulties obviously arise when any quantification of this distortion is difficult, such as the permanent distortion of a polarisable ion by surrounding ions. Also in this case 'model independent' methods have to be adopted in order to consider

contributions from repulsion between the non-spherical ions. So it can be seen that it is generally extremely difficult to make an estimate of  $\Delta_1$  for a crystal.

The major works that have attempted to estimate values for  $\Delta_1$  have done so by considering differences between Born-Haber ('experimental') and calculated lattice energies. Although this approach will obviously yield estimates of  $\Delta_1$  it will not give, as is often claimed, the magnitude of covalent contributions to bonding in the crystal (for a fuller discussion of this point see Phillips and Williams (1965)). The only method that could be used to obtain this quantity is to perform an ionic lattice energy calculation on a purely **ionic** crystal structure. The structure used for the ionic calculations in all work here and elsewhere is the equilibrium structure where covalency is present between the ions and is therefore affecting interionic distances, coordination numbers and atomic charges. This means the covalency has already been somewhat compensated for by the calculations (the extra energy of the 'bond' induced by the covalency is compensated for in the calculations by assuming pure ionic charges at partial covalent distances, which are shorter than for the pure ionic situation), and so  $\Delta_1$  is not an absolute measure of covalency in the crystal only a

measure of the instability of the pure ionic state, in the real lattice environment, with respect to the real crystal lattice. The prediction of covalent contributions to bonding in crystals would require the prediction of the crystal structures that would be shown by compounds if the bonding was purely ionic, and the comparison of a Born-Haber lattice energy with the lattice energy calculated from this structure.

The converse of the above argument would explain the difficulties encountered by attempts to predict crystal structures from lattice energy calculations (such investigations have failed to predict the relative stability of the sodium chloride and cesium chloride lattices, Tosi (1964)). The structures predicted are those that would exist if the bonding was purely ionic.

The work as described here contains no method of estimating  $\Delta_1$  or  $\Delta_2$ , they are assumed to be small in most cases, and are neglected. In families of salts where  $\Delta_1$  is liable not to be negligible, such as the alkaline earth chalcogenides, the trend in magnitude can be confirmed and thermodynamic parameters obtained from consideration of the most highly ionic members of the family.

#### Introduction

### 1.5 Empirical and Non-Empirical Calculation

The terms empirical and non-empirical are used loosely here as any current lattice energy calculation must be empirical in the true sense of the word because the forces existing between the ions in the lattice are not completely understood (apart from the electrostatic forces between spherically symmetrical monatomic ions). I am classifying 'non-empirical' calculations as those which require a precise knowledge of the full crystal structure and 'empirical' calculations as those that involve the application of an equation which only necessitates a knowledge of some properties of the ions which constitute the lattice, not of the relative arrangement of those ions.

The use of empirical calculations, although quite widespread in chemistry, is mainly the realm of inorganic chemists as a small part of a study of inorganic species by practical methods (mostly as a connecting link between the preparation and thermochemistry of a compound). The simple 'back-of-the-envelope' empirical approach is taken, generally because of its convenience, when not much emphasis is being placed on the method of calculation. Alternatively non-empirical methods tend to be used in

studies in which the major objective is to obtain the lattice energies themselves and little involvement with their inorganic implications is considered. The empirical approach when used because of the absence of full crystal structure data is invaluable, but its use when such data is available does not make full use of the attendant practical work and the results could be (unnecessarily) misleading.

It appears that what is needed is a 'non-empirical' approach which is as convenient to use as the empirical equations. One of the aims of this work is to provide an easy to use computer package for calculating lattice energies (using the latest 'non-empirical' method), hoping this will go some way to bridge the gap between inorganic and 'lattice energy' chemists. A merger of these two types of chemists would give more inorganic insight into the results obtained from lattice energies, something which is currently lacking in papers describing such calculations (including those in this study).

This section is not intended as a comprehensive review of methods to calculate lattice energies, but the inclusion of the most commonly used empirical equations, for comparison with the equations given in the method

#### Introduction



section, and an outline of the approach taken by the non-empirical methods is felt to be of value.

The main empirical equations in use today, and for the last thirty or so years, are those developed in the 1930's and 1940's by Kapustinskii (1932, 1943a,b). Recently work, mainly based in India, has been carried out experimenting with other forms of equations, however the work has not as yet proved to be of sufficient generality. The major criterion for an empirical approach to be useful is general applicability and this has only really been shown by the Kapustinskii method.

The Kapustinskii equation can have two forms (whose origin will become clear in the method section), of which the second is much more commonly used today.

$$U_{\text{POT}} = \frac{1080v|z_+||z_-|}{(r_+^+ + r_-^-)} \quad 1.5(i)$$

$$U_{\text{POT}} = \frac{1214v|z_+||z_-|}{(r_+^+ + r_-^-)} \left( 1 - \frac{0.345}{(r_+^+ + r_-^-)} \right) \quad 1.5(ii)$$

where  $|z_+|$ ,  $|z_-|$  are the moduli of the charges on the cation and anion,  $v$  is the number of ions in the formula unit and  $r_+^+$ ,  $r_-^-$  are the thermochemical radii of the cation

and anion (if these are in Angstroms the lattice energy is given in  $\text{kJ. mol}^{-1}$ ). Equation 1.5(i) is obtained assuming an inverse power form for the repulsive potential (with  $n=9$ , see section on repulsion energy) while Equation 1.5(ii) assumes the exponential form (with  $\rho=0.345^\circ$ , see section on repulsion energy). The assumption that is basic to the above equations is that every ionic compound, no matter what its real crystal structure, would have an identical lattice energy if it crystallised to form a sodium chloride type lattice. Although this is obviously not a fully justified assumption the agreement found with non-empirical calculations in most cases shows it to be reasonable.

The thermochemical radii are so called because for complex ions they are derived from thermochemical data; specifically the difference in lattice energy of two salts with a common complex ion may be equated to known thermochemical data to obtain the 'thermochemical' radius of the complex ion. For simple monatomic ions, such as the alkali metal cations, the Goldschmidt ionic radius is used for the thermochemical radius, this follows as the sum of cation and anion thermochemical radii should be the interionic distance in the proposed sodium chloride lattice. The work of Kapustinskii and Yatsimirskii has

produced fairly extensive tabulations of thermochemical radii for complex ions (Yatsimirskii (1947)(1948); Kapustinskii and Yatsimirskii (1949)).

I feel it is worth emphasising that the use of an experimental interionic distance in place of the sum of thermochemical radii in the Kapustinskii formulae is undesirable, unless of course the interionic distance comes from a sodium chloride type structure, as it neglects any change in this distance that would be necessary for the structure to be changed into the assumed sodium chloride lattice.

'Non-empirical' lattice energy calculations are based on a term-by-term approach. This considers the lattice energy to be made up as follows:

$$U_{\text{POT}} = U_{\text{ELEC}} - U_{\text{R}} + U_{\text{D}} \quad 1.5(\text{iii})$$

where  $U_{\text{ELEC}}$ ,  $U_{\text{R}}$  and  $U_{\text{D}}$  are the electrostatic, repulsion and dispersion energies respectively. This approach is the one used throughout this work, particular forms being taken for each energy term in Equation 1.5(iii), the result often being compared to those

obtained by the Kapustinskii equation. Each term will be dealt with in detail in the next section. A knowledge of the complete crystal structure is generally required for the evaluation of each term.

The calculation of lattice energies by quantum mechanical methods is not included here because, currently, it is not practically, or even theoretically, applicable to any but very simple salts (it has mainly been applied to lithium fluoride and other salts possessing the sodium chloride structure) and so it is not considered to be of a general enough nature.

#### 1.6 Lattice Energies from other Methods

On consulting Figure 1.3(ii), as was pointed out in Section 1.3, it is clear that estimating the lattice enthalpy is only one of three possible approaches that could be taken to solve the whole 'tetrahedral' cycle. The knowledge of the enthalpy of formation or hydration of the gaseous ions is also sufficient for solution, and hence for prediction of a value for the lattice enthalpy.

In some cases the enthalpies of formation of gaseous ions are known experimentally. The values for monatomic

cations are generally available (combining enthalpies of sublimation and ionisation potentials) and the values for halide ions are now virtually agreed upon (any remaining disagreement being in the electron affinity of halogen atoms). Few values however have been measured for complex ions, although the cyanide ion has received some attention (see for example Herron and Dohler (1960); Berkowitz, Chupka and Walter (1969)). Very recent work by Refaey (Refaey (1976); Refaey and Franklin (1976)) on ion-molecule collisions has led to values for the nitrite and nitrate ion and has given hope that in future experimental values for many more ions will become available.

The major method of estimating enthalpies of formation of gaseous ions, besides lattice energy calculations, is by quantum mechanical methods. These calculations are carried out by taking ideal geometries for the gaseous ions and calculating their total energy. They also yield charge distributions within the ion. However it is often found that calculations leading to 'good' thermochemical data do not also give 'good' charge distributions, and vice versa. This is a consequence of the approximations made in the various methods and casts some doubt on values which cannot be compared to other

#### Introduction

independently produced values. Generally work that uses these calculations does not apply the results obtained to the cycles considered here and so lattice energies are not predicted, although comparisons are often made with estimates of the thermochemical data (and charge distributions) produced by lattice energy work.

The sum of the hydration enthalpies of the ions which constitute the electroneutral lattice can be generally found if the enthalpies of formation of the gaseous ions is known, simply by the use of the enthalpy of formation of the aqueous ions (i.e. consideration of one of the 'unknown' faces of the tetrahedral cycle (Figure 1.3'ii)). The enthalpy of formation of most common aqueous ions (including complex) is experimentally known, although only relative to the hydrogen ion whose value is fixed at zero. This means a value for the sum of hydration enthalpies is only available in the few cases where enthalpies of formation of the gaseous ions are all known, mostly only simple metal halides.

The splitting of these sums of hydration enthalpies into values for individual ions is a subject that has received much attention. The difficulty of assigning individual ion values arises from the impossibility of

experimentally observing a process in solution that does not involve a counter ion. The easiest method is to define the hydration enthalpy of the hydrogen ion as zero. the ionic hydration enthalpies so obtained are called **conventional hydration enthalpies** and are most commonly quoted. Many workers, principally Noyes (1962), Halliwell and Nyburg (1963) and Morris (1968), have attempted to define sets of **absolute hydration enthalpies** for ions (i.e. assign a value for the proton), mainly by the use of empirical approaches to the sums of hydration enthalpies for the alkali halides. These approaches have been applied to spherical (or pseudo-spherical - rotating cyanide ion (Jenkins and Morris (1976))) ions where an ionic radius can be assigned.

The calculation, or estimation, of lattice energies by calculating sums of ionic hydration enthalpies has been attempted by three empirical approaches. All methods involve the plotting of sums of ionic hydration enthalpies versus a property of an ion or ions, for the alkali halides. These plots are found to be linear along the alkali halides with common ions, i.e. five lines are observed for lithium, sodium, potassium, rubidium and cesium. By measurement of the property for other ions or ion pairs and assuming that, for the same counter ion, the



same straight line will hold it is possible to obtain the sum of the ionic hydration enthalpies, and hence the lattice energy, for that ion-pair (i.e. ionic compound). The properties that have currently been used are the ionic radius (or 'crystal' radius) (Morris (1968), Jenkins and Morris (1977a)), the lyotropic number of the anion (see for example Buchner (1936,1950) and Waddington (1955)) and the viscosity B coefficient of the Jones-Dole equation (see Jenkins and Morris (1977b)). The similarities between the plots produced by the three methods indicate a definite connection between the properties.

The ionic radius method requires spherical ions, the lyotropic number method suffers from a lack of accuracy in measurement whilst the other method suffers from a lack of data. All assume the straight line relationship (shown conclusively for the halide ions) will hold for all ions, no matter their complexity (or shape). An assumption, although forced by lack of data, which one can hardly expect to be completely valid, and this must be remembered when lattice energies and thermochemical data obtained using these methods are compared to calculated values.

A common trap in the type of work above is to take consistency in predicted individual ion parameters, or in

#### Introduction



other values derived from these parameters, over a family of salts (lithium to cesium) to be evidence of the validity of the method. This agreement is forced as on analysis of all methods it can be seen that they simply predict one ion parameter from another (n.b. viscosity B values are said to be additive over ions, an ion contributing a fixed amount irrespective of the counter-ion) hence guaranteeing a consistent result over the family if all the data used is consistent. This is a common fault and explains the apparent 'astonishing consistency' that is sometimes obtained in the study of individual ion properties.

### **1.7 Aims of the Research**

The work, as described here, concentrates on certain parts of the large area covered in this introduction. Specific restrictions to note are:

- (a) the solution of the 'tetrahedral' thermochemical cycle (Figure 1.3(ii)) is via calculation of the lattice enthalpy and thermochemical data for ions is predicted by this approach;
- (b) the difference between the lattice energies calculated and 'true' values will, in most cases, be neglected, and to minimise errors incurred by this

approximation generally only alkali metal and ammonium salts are considered (mostly in compounds with anions having terminal halogen atoms) - these compounds should approximate to the pure ionic state:

(c) a 'non-empirical' approach is used for the calculation of the lattice energy, although often the results obtained are compared to those given by the 'empirical' equations.

Within the framework outlined above the most extensive general method for calculating lattice energies was adopted (see next section). This method involved several extremely 'uncertain' parameters which previously had to be estimated and also suffered from being difficult to apply to all but the simplest systems. The aims were mainly twofold. Firstly to remove completely, or at least minimise the effect of, any 'uncertain' parameters. Secondly to develop general techniques which could be finally embodied into a computer package capable of performing a lattice energy calculation for any ionic compound. This computer package should retain general applicability whilst possessing ease of use and a minimum of input data. Thus enabling its use by chemists unfamiliar with the full details of the necessary calculations performed within the package.

#### Introduction

During the course of the development of the method used in this computer package calculations on various families of salts have been carried out, and published as separate pieces of research. These calculations generally represent stages of the development of the method where a particular family of salts has been chosen, for various reasons, as a test to illustrate the use of the method at that stage. This is particularly well demonstrated by the calculations carried out on hexahalometallate(IV) salts (Jenkins and Pratt (1978) and alkali metal cyanides (Jenkins and Pratt (1977b)) at a stage when the method had only been quantified for cubic lattices. Other sets of calculations have been performed as they were necessary to gain information to be used in the further application of the method, such as the alkali halides (Jenkins and Pratt (1977a)).

## 2. Theory

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### 2.1 Term-by-Term Approach

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The lattice energy of an ionic compound can be visualised as the sum of the energies necessary to remove each of the ions in the formula unit from within a perfect infinite crystal of the compound to infinity. This description is the easiest to use when attempting to quantify all the necessary interactions.

In this research all interactions are assumed to be **pairwise additive**, i.e. the energy of a system is the sum of the energies of interaction of all the pairs. Jansen, in association with McGinnies and Lombardi (Jansen and McGinnies (1956a,b); Jansen and Lombardi (1964,1966)), has considered the inclusion of many body forces not only in lattice energy work but also more generally. There is little doubt that their inclusion makes the theory more complete but the quantitative results obtained appear little better or worse than those obtained using purely two body forces (e.g. see Jansen and Lombardi (1964) where the inclusion of many body forces fails to predict the

transition between the sodium and cesium chloride structures for the alkali halides). So at this stage the added complexity, which seems considerable, appears to have no justification and many body forces are not considered further in this research.

The description 'term-by-term' applies to the fact that the interaction between two charged bodies is assumed to be made up of different kinds of forces whose effects can be combined numerically in an additive fashion. The interaction energy ( $U_{INT}(ij)$ ) of two bodies (i and j) is assumed to be composed of the electrostatic ( $U_{ELEC}(ij)$ ), repulsion ( $U_R(ij)$ ) and dispersion ( $U_D(ij)$ ) energies, such that:

$$U_{INT}(ij) = U_{ELEC}(ij) - U_R(ij) + U_D(ij) \quad 2.1(i)$$

The lattice energy of an ionic compound ( $U_{POT}$ ), in the term-by-term framework, is the sum of all these pair interactions contributed to by a group of ions which constitute the formula unit:

$$U_{POT} = \sum_{pairs} U_{INT}(ij) \quad 2.1(ii)$$

Theory

implying

$$U_{\text{POT}} = \sum_{\text{pairs}} U_{\text{ELEC}}(ij) - \sum_{\text{pairs}} U_{\text{R}}(ij) + \sum_{\text{pairs}} U_{\text{D}}(ij) \quad 2.1(\text{iii})$$

and

$$U_{\text{POT}} = U_{\text{ELEC}} - U_{\text{R}} + U_{\text{D}} \quad 2.1(\text{iv})$$

which is the normal term-by-term formula (see Section 1.5).

The calculation of each term on the right hand side of Equation 2.1(iv) will now be dealt with in turn, followed by sections discussing the conditions which can be imposed on Equation 2.1(iv) and a description of the proposed new method.

## 2.2 Electrostatic Energy

In an ionic crystal the electrostatic energy is by far the most important contributor to the lattice energy and it provides the long-range order for the crystal. It is well known that the electrostatic energy of interaction

Theory

( $U_{ELEC}(ij)$ ) between two charges  $q_i$  and  $q_j$  separated by a distance  $R_{ij}$  is given by:

$$U_{ELEC}(ij) = \frac{-K q_i q_j}{R_{ij}} \quad 2.2(i)$$

where  $K$  is a conversion factor between  $e^2 \cdot \text{\AA}^{-1}$  and the appropriate energy units (taken as  $1389.10$  here to convert to  $\text{kJ} \cdot \text{mol}^{-1}$ ). Consequently the electrostatic energy of an ionic crystal can be represented as (noting the provisions of Equations 2.2(viii) and 2.2(ix)):

$$U_{ELEC} = \frac{-K}{2N} \sum_{i=1}^M \sum_{j=1}^M q_i q_j \sum_{k=1}^{n_i} \sum_{l=1}^{n_j} \frac{1}{R_{kl}} \quad 2.2(ii)$$

where  $N$  is the number of molecules per unit cell,  $M$  is the number of types of ion in the unit cell and  $n_i$  is the number of the  $i$ th type of ion in the unit cell. The last summation is over all ions of type  $j$  in the infinite lattice, excluding the terms where  $i=j$  and  $R_{kl}=0$ . The factor of one half is included as each interaction is considered twice.

Equation 2.2(ii) is more often expressed as:

$$U_{ELEC} = \frac{K M_1}{1} \quad 2.2(iii)$$

Theory

where  $M_1$  is called the Madelung constant based on the characteristic length  $l$ . It is so called after the first person to evaluate such a summation for an ionic crystal - Madelung (1918). It is referred to as a constant for when it is based on particular distances (cubic cell side or shortest interatomic distance) in simple lattices it can be merely a property of the type of structure. This is the case when all  $R_{kl}$  in Equation 2.2(ii) can be expressed as:

$$R_{k'l'} = k_{k'l'} l \quad 2.2(iv)$$

where  $k_{k'l'}$  is independent of  $l$  (the indices  $k$  and  $l$  have here been changed to  $k'$  and  $l'$ ). For example the Madelung constant, based on the cubic cell length, for the sodium chloride structure is 3.49513, and the electrostatic energy of any salt showing this structure may be computed directly from this value using the appropriate cell side (and if necessary any higher charge factor) in Equation 2.2(ii). This fact can be of interest in the comparison of types of structure and in the study of simple systems with high symmetry lattices. However in the study of more complex compounds, with complicated crystal structures, basing the Madelung constant on any



particular distance has no advantage. So in the few places where Madelung constants are mentioned in this research they will be based on unit distance and depicted by  $M_1$  where:

$$U_{\text{ELEC}} = K M_1 \quad 2.2(v)$$

The summation of Equation 2.2(i) is over an infinite series of  $1/r$  terms. It is a property of such series that even if they do converge, they do so very slowly if summed in an arbitrary fashion. There are two main approaches which have been used in order to obtain values for Madelung constants:

- (a) the terms in the series are arranged so as to form groups which are 'electrically neutral' and centered on one point. Under such conditions convergence is usually fairly rapid;
- (b) a mathematical transformation is applied to the summations, using the property of periodicity.

Reviews of the methods that have been evolved using these approaches are given by Waddington (1959) and Tosi (1964). This section contains only a guide to the major methods coupled with a mention of any recent related work.

#### Theory

The approach of rearranging the terms of the summations is perhaps best typified by the work of Evjen (1932) and Frank (1950). Very fast convergence is obtained for simple structures by these methods, however the securing of a Madelung constant for a complex structure requires much detailed analysis, and in complicated systems may not be possible. Another disadvantage is that often it is desirable to isolate the terms relating to a particular ion and this possibility is not present here because of the strict arrangement of the series that is required. All these reasons make the application of this technique undesirable and it is seldom used now for the calculation of Madelung constants.

The method of Madelung (1918), which was the first developed, is only applicable to highly symmetric systems and so has not been much applied. It involves the rearrangement of the terms into first electrically neutral rows, then grouping these into a plane and finally grouping the planes into a three dimensional lattice. However the terms are not summed directly as in the method of Evjen but the series is first subjected to Fourier transformation. Hence this method combines the two basic approaches.

#### Theory

The first really general approach developed was that of Ewald (1921, 1937). The only limitations are that the atoms have spherically symmetrical charge distributions and that the unit cell is electrically neutral. This second condition is necessary as each array of one type of ions is assumed to be balanced by a 'sea of electron density' of appropriate charge and these 'seas' must balance with each other. The approach uses a Fourier transform of the series, based on the property of periodicity. The point charges are replaced by spherically symmetric charge distributions centered at the atomic positions, these charge distributions were assumed to have a Gaussian nature. The replacement is perfectly valid if the atom is in a uniform field as it is allowed by the principles of electrostatics. The summation is split into two rapidly converging parts, one summation is carried out in real space and the other in reciprocal space. A parameter is present which allows varying emphasis on the two summations, and this is generally fixed at a value which provides optimum speed of convergence for both series.

The approach initiated by Bertaut (1952) again uses the method of Fourier transformation, replacing the point charges by a spherically symmetrical charge density. In

this case however only one summation results, that in the reciprocal lattice. It is necessary to correct the result for the self interaction energy of the atomic charge densities. Bertaut's method can be used with any spherically symmetrical charge density function and has been used with  $n=0,1,2$  and 3 in:

$$\sigma_n(r) = k(R-r)^n \quad R > r \quad 2.2(vi)$$

$$\sigma_n(r) = 0 \quad R < r$$

where  $\sigma_n$  is the charge density function,  $k$  is a normalising constant (for values see Waddington (1959)),  $R$  is the cut-off radius (fixed so there is no overlap of charge distributions in the lattice) and  $r$  is the distance from the atomic centre. A normalised Gaussian distribution:

$$\sigma_G(r) = k^3 \exp(-k^2 r^2) \quad \text{all } r \quad 2.2(vii)$$

(taken from Waddington (1959)) can also be employed, where a correction for the small amount of overlap must be made. In this case the Bertaut method has been shown

(Bertaut (1952)) to reduce to the Ewald method with the summation taken purely over the reciprocal lattice.

Recently Weenk and Harwig (1975) reported a minor error in the derivation of the Bertaut method while investigating electrostatic field gradients using this method. This criticism has however been dismissed as "having no serious basis" by Bertaut (1978) himself.

Williams (1971) has reported a more general derivation of the equations obtained by Bertaut, using summations over the lattice of  $r^{-n}$  terms. The Bertaut results are obtained when  $n=1$ . This work has importance in the calculation of dispersion energies (where  $n=6$  or  $8$ ).

A piece of work by Harris and Monkhorst (1969) may well provide a faster method than that of Bertaut or Ewald for the calculation of these summations, although so far it has only been applied to simple cubic systems. A Fourier transformation is involved but the point charges can be retained meaning that no distributed charge density has to be assumed. They have shown that this greatly simplifies the necessary calculations for the sodium and cesium chloride structures.

All the methods described thus far deal only with monopoles or their equivalent. If the restriction of spherical symmetry is removed terms resulting from the interaction of higher multipoles must be considered. Two distinct cases can be treated in this way. Firstly an ion whose electron density is permanently distorted by its non-symmetric environment of surrounding ions. Secondly a complex ion; which could alternatively be treated as an array of point charges and the methods previously described used. Jansen (1957) considered the interaction of two bodies and expressed the energy involved as a multipole moment expansion, each term depending on the magnitude of the relevant multipole moments. Neckel and co-workers (Neckel and Vinek (1964,1966); Neckel, Vinek and Nowotny (1967); Neckel, Kuzmany and Vinek (1971a); Neckel and Herzig (1977)) have used the Ewald method in conjunction with the work of Jansen to extend the approach to ionic solids. Initially (up to 1977) the work was only applicable to lattices with cubic or rhombohedral symmetry, although recently (Neckel and Herzig (1977)) it has been theoretically extended to all symmetries, and practically to tetragonal cases. Application (see work cited above plus Neckel, Kuzmany and Vinek (1971b) and Neckel, Herzig and Jenkins (1976)) has only been made to point charges distributed along an axis, i.e. complex ions

with cylindrical symmetry (or composed of such bodies), where the multipole moments are obtained by simple summation over the point charges. This means that effectively only monopoles are being considered still, and similar results are obtained using the methods previously described. This method, although having the disadvantage of requiring analysis of the structure prior to the calculations and some manipulation after, does have the advantage that as the electrostatic energy is expressed as a series expansion in terms of cell parameter(s) and a distance inside the 'multipole' it can be directly applicable to many different compounds with similar crystal structures (see the cubic hexahalometallate(IV) salts for a good example), when previous methods, as formulated, require re-calculation for each new compound. Particular forms of the expansion obtained using this method are given, where applicable, in the results section.

Blake (1977) has used the basic Bertaut method in his work on bodies not possessing spherically symmetrical charge distributions. He made a modification using charge density functions that approximate to the non-spherical systems, such as functions imitating p- or d-orbital symmetry. This modification requires a good knowledge of

the real situation in the ionic crystal, and some detailed analysis in obtaining the Fourier transforms of the charge density functions.

All work described here, and elsewhere, uses the 'infinite crystal' as a basic assumption, the one exception being the innovative work of Redlack and Grindlay (1972, 1975). Their approach is similar to the one taken by Harris and Monkhorst (1969) for an infinite crystal, but they produce results applicable to the finite crystal case, although they are restricted to certain shapes. Their final potential is split into two parts, one independent of the shape of the finite crystal (the 'intrinsic' potential) and one not (the 'extrinsic' potential). An important part of their work (1975) is that it is able to show the equality of all the methods discussed here in the infinite crystal limit, along with their applicability to the finite case. Unfortunately the approach has not been generally quantified as yet.

Another result of the work of Redlack and Grindlay (1975) is the proof that the potential term dependent on the shape of the finite crystal only vanishes in the infinite case if the net dipole and quadrupole moments of the unit cell are both zero. This establishes a situation

Theory



previously known to exist, that the potential of polar crystals is shape dependent and not correctly convergent. A fact which has prevented polar crystals being treated by, for example, the Bertaut method (the polarity means a loss of spherical charge symmetry on the ions) and it is hoped that the work of Redlack and Grindlay can be used to overcome this difficulty in the future. The work of Weenk and Harwig (1975, 1977a,b) on field strengths and gradients may also be of some use towards any improvements in this direction.

The treatment of complex ions as being arrays of point charges and not just spherical ions during the calculation of the electrostatic energy requires the assignment of how the total charge is distributed over the atoms in the ions. For reasons discussed in Section 2.7 it is advantageous not to assign the charge distribution at this stage. The maintaining of the charges as variable in Equation 2.2(ii) requires the selective evaluation of the summations following them. This causes added complications in the calculation of the electrostatic energy by the methods of Evjen, Frank, Madelung or those using similar approaches, and in many cases makes the attainment of a result improbable.

The choice of generally quantified approaches not excluded by the above is between those of Ewald, Bertaut and Neckel et al. The method of Neckel et al. has certain advantages and has been adopted in many studies during this research, especially in the early stages when other methods were not available. However the difficulties inherent in the general application of the method makes the choice of it unwise for major use at this time as alternative methods can now be used. The approaches of Ewald and Bertaut are both generally applicable and offer much of the same advantages. The method of Bertaut however requires the evaluation of only one series whilst that of Ewald requires two; this fact combined with the existence of a well written and established computer program (Blake (1973)) for the calculation of the electrostatic energy using the Bertaut method has led to it being used primarily throughout this work and as a basis for the computational extensions executed. Section 2.7 gives the symbolic representation of the Bertaut method.

When a complex ion is treated as an array of point charges for the calculation of an electrostatic energy the value resulting is the energy (electrostatic) necessary to decompose the lattice into these point charges. As was pointed out in Section 1 we require the complex ions to

remain intact throughout the process and so we need to correct this electrostatic energy (often referred to as the **Madelung energy**) by the **self energy** of the complex ions in order to obtain the true **electrostatic energy** of the lattice. Each complex ion in the unit cell has a self energy, the total self energy of the ions,  $U_{SE}$ , is given by:

$$U_{SE} = \frac{K}{N} \sum_{i=1}^M \sum_{j=1}^{n_i} \sum_{k=1}^{m_i} \sum_{l=k+1}^{m_i} \frac{q_{ik} q_{jl}}{R_{ikl}} \quad 2.2(viii)$$

where  $m_i$  is the number of point charges in the ion of type  $i$ . It should be noted that the summations over types of ion in Equation 2.2(ii) are really over partial ions and the energy given is really the Madelung energy,  $U_M$ . The true electrostatic energy is given by:

$$U_{ELEC} = U_M + U_{SE} \quad 2.2(ix)$$

The desire to improve the speed (and in some cases the possibility) of convergence of the summations in Equation 2.2(ii) are the reason for the introduction of mathematical methods. Consequently claims, and counter claims, have been made about the relative efficiencies of

the various methods proposed, both by the proposers and users. To a certain degree now these claims are becoming irrelevant. The general availability of modern high-speed computers has led to comparatively cheap computer time and consequently lessened the need to make rapidity of convergence the sole criterion. A much more important aspect these days is program efficiency and general applicability, with lattice symmetry used to maximum advantage. It is however essential to be aware of the degree of convergence obtained and work has been performed which estimates this for the Bertaut method (Templeton (1955); Templeton and Jones (1956); Jenkins (1971, 1973)). The latter enables relationships between extent of summation and the number of decimal places of convergence to be obtained.

In summary it is possible to compute exactly the electrostatic energy of an ideal ionic crystal within the framework of the following assumptions and provisions:

- (a) the crystal can be assumed infinite;
- (b) the bodies giving rise to the forces can be assumed to be pure monopoles, with all higher multipoles zero (i.e. a point charge);
- (c) the unit cell, and hence macroscopic crystal, has no nett dipole moment;

#### Theory

(c) the values of all the point charges in (b) are known or can be established (see Section 2.7).

### **2.3 Repulsion Energy**

The electrostatic forces described in the preceding section would cause the lattice to collapse if they were the only forces present. To prevent this collapse the interatomic forces must become repulsive at distances shorter than those found at equilibrium. This short range repulsion can be understood within the framework of the exclusion principle; the overlap between two closed electron shells of adjacent atoms is unfavoured and leads to a repulsive force between the atoms. For simple systems, primarily two hydrogen atoms with parallel spins or two helium atoms, first-order perturbation theory can be used to estimate the magnitude of the repulsive force (Slater (1928); Fosi (1964)). But for more complicated cases, like those considered in this research, it is not possible to make any reasonable estimate from first principles.

The approach that was adopted in the early attempts to estimate the repulsive contribution to the lattice energy was to assume a simple functional dependence on the

Theory

interatomic distance, determining the parameters of this dependence by fitting the potential to known experimental factors and conditions (see Sections 2.5 and 2.6).

The first functional form chosen was a simple inverse power:

$$U_R = \frac{B}{r^n} \quad 2.3(i)$$

and was used primarily by Born and Lande (1918) and Born (1926). In Equation 2.3(i)  $r$  is the shortest anion-cation distance in the lattice and  $B$  and  $n$  are variable parameters (although Born and Lande (1918) initially tried to assign  $n$  from atomic theory).

The advent of quantum mechanics led to the numerical calculation of the repulsive energy between simple atoms mentioned earlier. In these cases the repulsion energy was seen to have an exponential dependence on interatomic distance and so a function of the form:

$$U_R = B \exp(-r/\rho) \quad 2.3(ii)$$

Theory

was adopted (Born and Mayer (1932)) in preference to the inverse power form.  $B$  and  $\rho$  are now the variable parameters.

Despite some recent work (Thakur (1976) proposed a logarithmic form) the exponential decay of the repulsion energy with interatomic distance is still accepted as the most appropriate form. Equation 2.3(ii) however, as it contains only **one** exponential term, only includes (explicitly) repulsion between nearest neighbours at a distance  $r$ . In many ionic lattices repulsions between other ions are important and so a better form was developed (Huggins and Mayer (1933); Huggins (1937)) which included repulsions between ions up to the next-nearest neighbours. Today this has been extended to include contributions from all possible ion pairs in the lattice.

To avoid the proliferation of variable parameters when moving from the simple form of Equation 2.3(ii) to an expression which would include repulsion between all pairs of ions steps had to be taken to make the variable parameters included as universal as possible. In most work the assumption that  $\rho$  is, at least, constant over all the interactions in a particular crystal is made (exceptions to this can be made where extensive experimental data is

available, mainly for the alkali halides, see Baughan (1959), Fumi and Iosi (1964a,b) and Gilbert (1969)). The parameter  $B$  is split into a universal proportionality factor and factors depending on properties of the interacting ions. These ion properties are a characteristic length (or radius), ionic charge and the number of valence electrons; all of which intuitively will effect the repulsion between the two ions. The characteristic radius first used (Born and Mayer (1932)) was the ionic radius of Goldschmidt (1926), however Huggins and Mayer (1933) used experimental data to obtain a set of radii consistent with the choice of the other parameters, they called these 'basic' or constant-energy radii. This form of repulsion energy, though not with the original 'basic' radii, is the one adopted in this work.

The general repulsion energy between two ions  $i$  and  $j$  ( $U_R(ij)$ ) is written:

$$U_R = b \sigma_{ij} \exp \left( \frac{\bar{r}_i + \bar{r}_j - R_{ij}}{\rho} \right) \quad 2.3(111)$$

where

$$\sigma_{ij} = 1 + \frac{q_i}{p_i} + \frac{q_j}{p_j} \quad 2.3(1v)$$

Theory



where  $\bar{r}_i$  is the 'basic' radius of ion  $i$  (hereafter the quotes around the word basic are omitted),  $p_i$  is the number of valence electrons of ion  $i$ ,  $R_{ij}$  is the distance between the ions and  $b$  is the universal constant (taken as  $10^{-12}$  erg.molecule $^{-1}$  in all work here following Huggins (1937)). The parameter  $c_{ij}$  was first introduced by Pauling (1928) to account for the charge dependence of the repulsion energy.

Using the above general approach the expression used to calculate the repulsion energy contribution to the lattice energy is as follows:

$$U_R = \frac{b}{2N} \sum_{v=1}^N \sum_{j=1}^M c_{vj} \exp\left(\frac{\bar{r}_i + \bar{r}_j}{P}\right) \sum_{k=1}^{n_i} \sum_{l=1}^{n_j} \exp\left(\frac{-R_{kl}}{P}\right) \quad 2.3(v)$$

where  $N$  is the number of molecules per unit cell,  $M$  is the number of types of ion in the lattice and  $n_i$  is the number of  $i$  ions in the unit cell.

The factor of one half is included in Equation 2.3(v) to prevent each pair interaction being included twice. The last summation is over all  $j$  ions in the infinite lattice, not including terms internal to complex ions. Specific

examples of this equation are given in the results section.

Equation 2.3(v) is designed primarily to deal with lattices composed of spherical bodies where a basic radius can be assigned to each ion or atom. Extension can be made to include non-spherical repulsion envelopes, specifically Gray and Waddington (1956), Waddington (1958), Jenkins, Dixon and Waddington (1971, 1972) have considered the azide and bifluoride ions as ellipsoids. This general approach requires the assignment of a characteristic length for the non-spherical body in every possible direction. This complexity makes its application fraught with uncertainty, and is hence prone to error. Work is described here (also Jenkins and Pratt (1977a,b)) which circumvents the necessity of using this approach while using the form of Equation 2.3(ii) for the repulsion energy.

The numerical evaluation of the repulsion energy using Equation 2.3(v) requires the knowledge of the full crystal structure of the compound under study, together with some properties of the constituent atoms and ions. The number of valence electrons of a complex ion is also required if the ion is to be treated as being spherical. This property is difficult to estimate but the effect of

this parameter is small and it is usually taken as that for most monatomic ions (eight). By far the largest influence on the repulsion energy are the basic radii, which are also the least well understood. It is necessary to obtain these radii by fitting lattice energy calculations to experimental data. Huggins (1937) originally obtained values for the alkali metal and halide ions and later, with Sakamoto (1957), for the alkaline earth metal and chalcogenide ions. Fumi and Iosi (1964a,b) also report values for the alkali metal and halide ions. Work included in this research (Jenkins and Pratt (1977)) has obtained values compatible with the method described in this theory section. Before the advent of the method developed in this research, radii for ions which were neither simple nor monatomic had generally to be estimated, leading to corresponding errors in the lattice energies obtained. It is now possible to calculate values for basic radii for a variety of models of a complex ion made up of identical sized spheres.

The structurally dependent summation required in Equation 2.3(v) is readily performed by direct summation owing to rapid convergence. Such summations converge much faster than either of the dispersion summations, see Figure 2.4(i).

#### Theory

## 2.4 Dispersion Energy

Dispersion forces (so called because of their dependence on dispersion f-values) were first recognised, and named, by London (Eisenschitz and London (1930); London (1936a,b)). The forces are also known as London, Van der Waals or correlation forces. Their existence was postulated to explain the fact that inert gases form condensed phases, no other interatomic attractive forces (Coulombic, 'covalent' or 'metallic' bonding) being present. They arise because of the correlation of electron motion between two atoms, ions or molecules. A semi-classical explanation is that at a given moment an otherwise spherically symmetrical atom will have an instantaneous dipole moment due to there being a slightly greater electron density on one side of the atom. This dipole is constantly changing due to electron motion. The spherical symmetry means the time average of this dipole is zero. The instantaneous dipole induces a further dipole in an adjacent atom (the magnitude of which depends on the polarisability of the adjacent atom) which gives rise to an attractive force between the atoms. Similar forces will be present between instantaneous and induced dipoles and quadrupoles, quadrupoles and quadrupoles, and all such combinations of multipoles; although the magnitude of

Theory

these forces reduces quite sharply with the joint complexity of the multipoles. In an ionic crystal such forces are present between each pair of ions (and atoms).

The origin of the forces means quantum mechanical methods must be employed to obtain the simple formulae necessary to generally quantify them (*ab initio* calculations are only possible for simple systems such as hydrogen and helium). Derivation of these formulae involves approximations such as:

- (a) multipole expansion of the interaction Hamiltonian;
- (b) the use of simple product zero-order wave functions;
- (c) one absorption dominates the absorption spectrum.

These approximations make quantitative predictions from the formulae obtained quite inaccurate. This inaccuracy seems unavoidable at this stage. All one can do is to attempt to choose the parameters used as carefully as possible and remain aware of the quality of the results obtained. The effect any inaccuracy in this term has on the lattice energy calculated is considered in Section 2.6, though it should be said here that the possible errors induced are not prohibitive.

Excellent reviews of the origin of dispersion forces

Theory

and the methods of obtaining the formulae below are given by Pitzer (1959) and Margenau and Kestner (1971). A full discussion of the consequence of these forces in lattice energy calculations is given by Tosi (1964).

If the nature of dispersion forces is investigated by second order perturbation theory the results of London (1930a,b) are obtained. The force is found to be of a two-body nature with an expression for the dipole-dipole attractive dispersion energy between atoms 1 and 2 of (as quoted by Tosi (1964)):

$$U_{dd}(12) = \frac{6}{R_{12}^6} \sum_{i,j} \frac{(\mu_{1i}^{oi})^2 (\mu_{2j}^{oj})^2}{\epsilon_1^{oi} + \epsilon_2^{oj}} \quad 2.4(1)$$

where  $U_{dd}(12)$  is the dipole-dipole dispersion energy,  $R_{12}$  is the distance between atoms 1 and 2, the sum is over the excited states of both atoms,  $\mu_{1i}^{oi}$  is the matrix element of the x component of the dipole moment of atom 1 between the ground state and the  $i$ th excited state and  $\epsilon_1^{oi}$  is the energy of atom 1 in the  $i$ th excited state relative to the ground state. The assumption that one term of the summation predominates (i.e. both atoms show one dominant excited state) leads to the familiar formula:

$$U_{dd}(12) = \frac{3}{2} \frac{d_1 d_2 \epsilon_1 \epsilon_2}{R_{12}^6 (\epsilon_1 + \epsilon_2)} \quad 2.4(11)$$

Theory

for the pair interaction energy: where  $d_1$  is the polarisability of atom 1 and  $E_1$  is known as the characteristic energy of atom 1.

Margenau (1931) developed a similar single level formula for the dipole-quadrupole dispersion energy ( $U_{qd}$ ) which for the same pair of atoms takes the form:

$$U_{qd}(12) = \frac{9}{4} \frac{U_{dd}}{e^2 R_{12}^2} \left( \frac{d_1 E_1}{p_1} + \frac{d_2 E_2}{p_2} \right) \quad 2.4(iii)$$

where  $e$  is the electronic charge and  $p_1$  is the effective number of electrons in atom 1. It can be seen that the dipole-quadrupole term has a  $R^{-8}$  dependence. A quadrupole-quadrupole term has been investigated by Margenau (1939) but is not considered here, it has a  $R^{-10}$  dependence.

Dispersion forces may also be investigated by the variational method, this was done by Slater and Kirkwood (1931) who obtained the following approximate result:

$$U_{dd}(12) = \frac{3d_1 d_2}{2R_{12}^6} \left[ \left( \frac{d_1}{N_1} \right)^{1/2} + \left( \frac{d_2}{N_2} \right)^{1/2} \right] \frac{h}{2\pi m \omega} \quad 2.4(iv)$$

where  $h$  is Planck's constant and  $m$  is the electron mass, and

where  $N_1$  is the number of electrons in the outer subshell of atom 1. The corresponding formula for the dipole-quadrupole term has recently been obtained by Naryan (1977) as:

$$U_{qd}(12) = \frac{27}{8} \frac{d_1 d_2}{R_{12}^8} \frac{\left[ \left( \frac{d_1}{N_1} \right)^{1/2} + \left( \frac{d_2}{N_2} \right)^{1/2} \right]}{\left[ \frac{d_1}{N_1} + \frac{20}{3} \left( \frac{d_1 d_2}{N_1 N_2} \right)^{1/2} + \frac{d_2}{N_2} \right]} \frac{h^2}{4\pi^2 m} \quad 2.4(v)$$

A seldom used formula for the dipole-dipole dispersion term was formulated by Muller (1936), for his work on paraffins, involving the diamagnetic susceptibility ( $\chi$ ):

$$U_{dd}(12) = \frac{6mc^2 d_1 d_2}{R_{12}^6} \left[ \left( \frac{d_1}{\chi_1} \right) + \left( \frac{d_2}{\chi_2} \right) \right] \quad 2.4(vi)$$

where  $m$  is the electronic mass and  $c$  the velocity of light.

Some fairly recent work by Winslow (1975) has treated the calculation of dispersion energies with more theoretical rigour. He used an adaptation of the Slater and Kirkwood approach and considered all, and not just valence, electrons. The limited number of dipole-dipole dispersion coefficients he quotes are all slightly greater than those obtained by Mayer (1933a) using London's



formulae, but the difference is not particularly alarming. However it must be noted that his related dipole-quadrupole coefficients are significantly larger than Mayer's. Winslow's work may lead in the future to more accurate dispersion energy calculations for ionic compounds.

The different approaches given above lead to quite different results for systems where parallel calculations have been performed (Pitzer (1959)). This shows the degree of inaccuracy that is present in the calculation of these terms. Over the years since the development of the parallel theories the London formulae have been most widely used, and this approach is used in the present studies.

A further approximation made in this research is that:

$$U_D = U_{dd} + U_{qd} \quad 2.4(vii)$$

higher terms being neglected. The terms can be written for an ionic crystal as:

$$U_{dd} = \frac{1}{2N} \sum_{i=1}^N \sum_{j=1}^N C_{ij} \sum_{k=1}^{n_i} \sum_l^{n_{js}} (R_{kl})^{-6} \quad 2.4(viii)$$

Theory

and

$$U_{qd} = \frac{1}{2N} \sum_{i=1}^n \sum_{j=1}^n Q_i \sum_{k=1}^{n_i} \sum_{l=1}^{n_j} (R_{kl})^{-8} \quad 2.4(ix)$$

where

$$C_{ij} = \frac{2 e^4 Q_i Q_j}{3(\epsilon_i + \epsilon_j)} \quad 2.4(x)$$

$$D_{ij} = \frac{3}{2} C_{ij} \left( \frac{Q_i}{p_i} + \frac{Q_j}{p_j} \right) \quad 2.4(xi)$$

and

$$Q_i = \frac{3d_i \epsilon_i}{2e^2} \quad 2.4(xii)$$

also  $N$  is the number of molecules per unit cell,  $M$  is the number of types of ion in the unit cell and  $n_i$  is the number of  $i$  ions in the unit cell.

The factor of one half is included in Equations 2.4(viii) and 2.4(ix) to avoid each pair interaction being taken twice. The first two summations in these equations

#### Theory

are over the types of ions, the third is over all the ions of type  $i$  in the unit cell whilst the last is over all ions  $j$  in the infinite crystal (i.e. the interaction between an individual atom  $i$  and **all**  $j$  ions), not including the internal terms of complex ions. Specific examples of Equations 2.4(viii) and 2.4(ix) are given in the results section.

The above equations owe much to the work of Mayer (1933a).

The numerical evaluation of the dispersion energy of an ionic solid, according to the above equations, requires the knowledge of the full crystal structure and the assignment of three parameters for each type of atom or ion being considered. Of these three parameters the polarisability has by far the largest effect on the value of the dispersion energy. The most commonly used method for obtaining polarisabilities for ions is the analysis of the refractive index of ionic solids, although other methods have been used leading to similar results. An analysis led to the conclusion that the most reliable set of values is that given by Piranne and Kartheuser (1964) although the work of Tessman, Kahn and Shockley (1953) and Pauling (1927) are more often quoted due to the larger

#### Theory

number of ions (both monatomic and complex) for which they quote polarisability values. Despite the fact that individual values can differ quite greatly from set to set similar values for dispersion energies in an ionic solid are obtained if a consistent set is used for all ions in the lattice (the approach adopted here).

The characteristic energy of an ion is defined as the energy of the absorption maximum of the ion in the ultra-violet. Often a good approximation is to take the ionisation potential of the ion, or a simple factor of it (Mayer (1933a) used 0.75 of the ionisation potential, now 0.9 is more commonly used). It does not seem worthwhile obtaining more accurate values for the characteristic energy as its appearance in Equation 2.4(ii) is merely the result of an approximation, the validity of which Pitzer (1959) has brought into question. The effect of such parameters on the dispersion energy is fortunately fairly small.

The third parameter, the effective number of electrons of the ion, has a small effect and this merely on the dipole-quadrupole dispersion energy, itself a small contribution to the total dispersion energy. Consequently accurate estimates of its value are unnecessary and

#### Theory

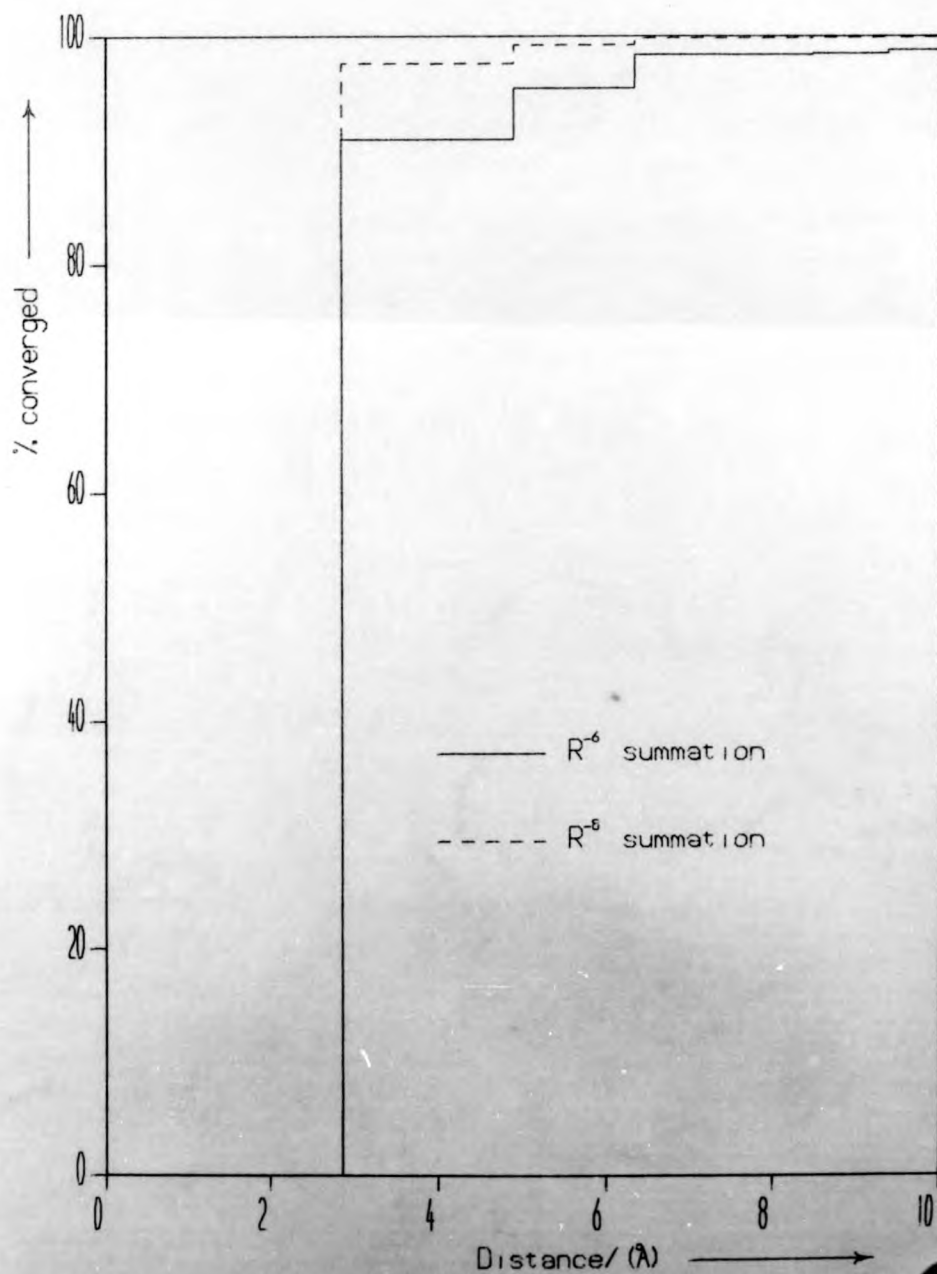
normally it is taken as the number of valence electrons (generally two or eight). Mayer (1933a) considered the geometric mean of the number of valence electrons and the number of electrons necessary to account for the polarisability, on the one-level approximation, to be the best estimate. The latter value being given by:

$$p_i = \frac{4\pi^2 m \epsilon_i^2}{e^2 h^2} \quad 2.4(xiii)$$

where  $h$  is Planck's constant.

The summations of inverse power functions of interatomic distances in Equations 2.4(viii) and 2.4(ix) can be easily computed by direct summation over the real lattice. Work by Williams (1971) has applied similar techniques to those used in the evaluation of Madelung constants in order to accelerate convergence. These techniques however are not used here as it is felt that the additional complications introduced are not justified by the small savings in computer time that would result. The summations are generally rapidly convergent, as is shown by Figure 2.4(i) where the sodium chloride summations in sodium chloride are used as an example. Here both series are over 95% converged by consideration of

Figure 2.4(i) Convergence of the dispersion energy summations.



atoms inside a  $10^9$  sphere (although in practice, and throughout this research, summations are extended well beyond this limit). Williams' work involves repetitious evaluation of these summations over the structures of paraffins, where the convergence is much slower, and in this case any convergence acceleration leads to appreciable savings in computer time.

It is obvious that the use of approximate formulae with approximate ion parameters must lead to, at best, only rough estimates being made for the dispersion energy term. This is one of the two main sources of possible error in the calculation of lattice energies as presented here. Errors in the dispersion energy need not however be directly transferred to the lattice energy (see later).

## 2.5 Energy Minimisation

The principle that the energy of an ionic solid must be at an energy minimum is intuitively obvious. This minimum, with respect to the unit cell volume, can be shown from the simple equation of state for a static cubic solid with the harmonic approximation, at negligible pressure (such as atmospheric) (Tosi (1964)). It is also confirmed by more detailed equation of state studies by

Fumi and Losi (1962, 1963).

The fact that the energy of a solid is a minimum means the lattice energy must be a **maximum** when defined as in Section 1.2. A very common, if unimportant, mistake is to refer to lattice energy minimisation; this mistake is even made in some published parts of this research. Mathematically the lattice energy is shown to be a maximum in the next section.

The extension of the idea of minimisation with respect to the unit cell volume to other variable parameters of the crystal structure is desirable and certainly appears valid. The possible variables are:

- (a) the space group;
- (b) the unit cell parameters (where applicable, i.e. not determined by the space group symmetry);
- (c) the atomic positions (where applicable).

The case of (a) appears difficult to quantify at the present time, at least at first sight, the others would appear straightforward. The necessity of keeping the geometry of complex ions rigid has led to minimisation with respect to the unit cell lengths **only** being quantified in this research. Further extension must merely

Theory



be a matter of time.

The minimisation may be represented by:

$$\left( \frac{\partial U_{POT}}{\partial i} \right)_{i=i_0} = 0 \quad 2.5(i)$$

where  $i$  is the parameter with respect to which maximisation is taking place and  $i_0$  is its equilibrium value (in this research  $i = a, b$  or  $c$ , the unit cell lengths). This implies, from Equation 2.1(iv), that:

$$0 = \left( \frac{\partial U_{ELEC}}{\partial i} \right)_{i=i_0} - \left( \frac{\partial U_R}{\partial i} \right)_{i=i_0} + \left( \frac{\partial U_D}{\partial i} \right)_{i=i_0} \quad 2.5(ii)$$

If we define a simple cubic lattice as one which contains no complex ions then we can say, for any distance  $R$  in the lattice:

$$R = ka \quad 2.5(iii)$$

where  $k$  is independent of  $a$  (the cubic cell side), this makes minimisation of the energy of this lattice straightforward and it has been fully performed from the

Theory

beginning of lattice energy calculation.

The consideration of non-cubic lattices has begun since the availability of high-speed computers. Neckel, Vinek and Vowotny (1967) considered the specific case of tetragonal carbides. The pioneering work of Williams (1965a,b, 1966a,b, 1967, 1969, 1970, 1971, 1972a,b, 1974) and Williams and Starr (1977) in the application of a general method (similar to the one presented here although developed entirely separately) to the prediction of crystal structures of hydrocarbons has been adapted by Busing (1970, 1972) to the study of ionic cases, specifically some alkaline earth halides and lithium tetrafluoroberyllate. Williams' and Busing's work utilises the condition of minimum energy with respect to crystal structure parameters in order to calculate them from a lattice potential similar to the one adopted from previous sections. The degree of success in predicting ionic crystal structures is however somewhat debatable, although it should be stated that the approach produces better results than any previous to it. Busing's work also forms the basis for some work by Murfitt (1971) on the sulphate and phosphate ions, by Yuen, Murfitt and Collin (1974) on alkaline earth halides and by Yuen, Lister and Nyberg (1977) on calcite and aragonite. The method developed by

Theory

these various workers (from Busina to Yuen et al), although only applied to the few systems mentioned above, shows much promise as a general method to rival the one developed in this research. It uses experimental crystal structure properties to obtain parameters for a simple two-body potential by a least squares fit (minimisation of the residual function), the opposite to the approach for which the method was first developed. The results for potential parameters found by Yuen et al (1977) for calcium carbonate are at variance with previously used values, especially with regards to dispersion energy parameters and their equivalent to ionic radii, it is hoped that this disagreement can soon be rectified. Work is now under way in this laboratory investigating this point.

The inclusion of complex ions in the simple cubic lattice has only been considered by Jenkins and Waddington (1975a) and Jenkins (1976a). Such limited applications stem from the desire to produce simple equations, sacrificing strict general applicability for simplicity. A general approach is presented in Section 2.7.

The derivation of the simple lattice energy equations using the simple cubic case follows. Other derivations use maximisation with respect to the shortest anion-cation

#### Theory

distance rather than the cubic cell length. This is done in order to make the transition to the general case appear simple. The derivations are however completely equivalent by virtue of Equation 2.5(ii). The three derivatives of Equation 2.5(ii) are required, in this case:

$$U_{\text{ELEC}} = \frac{K M a}{a_0} \quad 2.5(\text{iv})$$

consequently:

$$\left( \frac{\partial U_{\text{ELEC}}}{\partial a} \right)_{a=a_0} = \frac{-K M a}{a_0^2} = \frac{-U_{\text{ELEC}}}{a_0} \quad 2.5(\text{v})$$

The dispersion energy is assumed to be composed as Equation 2.4(vii) so in this simple case it can be expressed:

$$U_D = \frac{C}{a_0^6} + \frac{D}{a_0^8} \quad 2.5(\text{vi})$$

where C and D are independent of a, giving:

$$\left( \frac{\partial U_D}{\partial a} \right)_{a=a_0} = \frac{-6C}{a_0^7} - \frac{8D}{a_0^9} \quad 2.5(\text{vii})$$

$$= \frac{-6U_{dd}}{a_0} - \frac{8U_{qd}}{a_0} \quad 2.5(\text{viii})$$

Theory

If the repulsion energy is given the inverse power form (Equation 2.3(i)) then:

$$\left( \frac{dU_R}{da} \right)_{a=a_0} = \frac{-n U_R}{a_0} \quad 2.5(ix)$$

using Equation 2.5(iii).

Substituting into Equation 2.5(ii) leads to:

$$U_R = \frac{1}{n} (U_{ELEC} + 6 U_{dd} + 8 U_{qd}) \quad 2.5(x)$$

hence

$$U_{POT} = U_{ELEC} (1 - 1/n) + U_{dd} (1 - 6/n) + U_{qd} (1 - 8/n) \quad 2.5(xi)$$

This is the extended Born-Landé equation and when dispersion terms are neglected gives the simple Born-Landé equation:

$$U_{POT} = U_{ELEC} (1 - 1/n) \quad 2.5(xii)$$

Theory

If the repulsion energy is expressed in the exponential form of Equation 2.3(ii) then:

$$\left( \frac{\partial U_R}{\partial a} \right)_{a=a_0} = \frac{-r_0}{a_0^9} U_R \quad 2.5(xiii)$$

where  $r$  is the shortest anion-cation distance. Leading to:

$$U_R = \frac{e}{r_0} (U_{ELEC} + 6 U_{dd} + 8 U_{qd}) \quad 2.5(xiv)$$

and:

$$U_{POT} = U_{ELEC} (1 - e/r_0) + U_{dd} (1 - 6e/r_0) + U_{qd} (1 - 8e/r_0) \quad 2.5(xv)$$

which is the extended Born-Mayer (or Ladd and Lee (1958)) equation. If dispersion terms are neglected the simple Born-Mayer equation results:

$$U_{POT} = U_{ELEC} (1 - e/r_0) \quad 2.5(xvi)$$

Adoption of the Huggins-Mayer form for the repulsion

Theory

energy (Equation 2.3(v)) doesn't lead to a simple equation. It is considered, for a general lattice, in Section 2.7.

Inspection of Equations 2.5(xii) and 2.5(xvi) shows quite clearly the reason for the form of the Kapustinskii equations (see Equations 1.5(i) and 1.5(ii)). The shortest anion-cation distance being replaced by the sum of ion radii.

If there are complex ions present in our simple cubic lattice then though we can maintain Equation 2.5(iii) as regards the evaluation of the repulsion and dispersion energies, by choice of suitable models (see Section 2.6), we cannot do this for the electrostatic energy if the complex ion possesses internal structure. In this latter case Equation 2.5(v) becomes:

$$\left( \frac{\partial U_{\text{ELEC}}}{\partial a} \right)_d = \frac{-U_{\text{ELEC}}}{a_0} + \frac{K}{a_0} \left( \frac{\partial M}{\partial a} \right)_d \quad 2.5(\text{xvii})$$

where the suffix d is included to indicate the rigid geometry of the complex ions (it signifies an internal distance vector). This is the case considered by Jenkins and Waddington (1975a) and Jenkins (1976a), their results

are, in general forms:

$$U_R = \frac{e}{r_o} \left[ U_{ELEC} + 6 U_{dd} + 8 U_{qd} - K \left( \frac{\partial M_a}{\partial a} \right)_d \right]_{a=a_o} \quad 2.5(xviii)$$

and

$$U_{POT} = U_{ELEC}(1 - e/r_o) + U_{dd}(1 - 6e/r_o) + U_{qd}(1 - 8e/r_o) + \frac{e}{r_o} \left( \frac{\partial M_a}{\partial a} \right)_d \bigg|_{a=a_o} \quad 2.5(xix)$$

These workers expressed the electrostatic energy in the form of a multipole moment expansion. The above equations correct an error in their work, they quote  $a_o$  in place of  $r_o$  throughout as a consequence of adopting the cell constant in the repulsion energy expression rather than the shortest anion-cation distance.

In most cases Equation 2.5(iii) does not hold and all the above equations, although useful as approximations, are not generally valid, since terms involving derivatives of interatomic distances must, at least, be included. No simple formulae can be obtained by this general approach.

The technique of energy minimisation, as it involves no extra parameters, introduces no errors. On the contrary

Theory



its very nature is such that it can be used to lessen possible errors (see Section 2.8). The minimisation with respect to more parameters means the imposition of extra constraints on the potential and can only lead to improved values for lattice energies.

## 2.6 Compressibility of a Solid

The equation of state of a static cubic solid under the harmonic approximation yields the result (Tesi (1964)):

$$\frac{d U_{\text{POT}}}{d V_m} = P \quad 2.6(1)$$

where  $V_m$  is the molar volume and  $P$  the pressure. This equation, if the pressure is negligible, gives the minimum energy condition used in the previous section. On further differentiation and replacing the molar volume by the unit cell volume,  $V$ , one obtains:

$$\frac{d^2 U_{\text{POT}}}{d^2 V} = \frac{-1}{\beta V} \quad 2.6(11)$$

where  $\beta$  is the coefficient of isothermal

Theory

compressibility of the solid (and is positive showing the principle of a lattice energy maximum). This equation has great theoretical value in that it provides yet another constraint on the potential form (enabling, theoretically, the evaluation of the repulsion exponent, see later). However its practical application is limited owing to two major restrictions:

- (a) in all but cubic systems the compressibility of the solid is anisotropic and no simple relationship like Equation 2.6(ii) holds;
- (b) even in the case of salts showing cubic symmetry compressibility data is not commonly available, and what data that exists has variable reliability.

Despite these difficulties Equation 2.6(ii) has been used in consideration of the simple cubic case (discussed in the last section) to derive equations for the establishment of values for the repulsion exponent. First we must note that:

$$\frac{\partial^2 U_{\text{POT}}}{\partial v^2} = \frac{1}{9a^4} \frac{\partial^2 U_{\text{POT}}}{\partial a^2} \quad 2.6(iii)$$

Following on from the previous section:

$$\left( \frac{\partial^2 U_{\text{ELEC}}}{\partial^2} \right)_{a=a_0} = \frac{2U_{\text{ELEC}}}{a_0^2} - \frac{2K}{a_0^2} \left( \frac{\partial H_0}{\partial a} \right)_{a=a_0} + \frac{K}{a_0} \left( \frac{\partial^2 H_0}{\partial a^2} \right)_{a=a_0} \quad 2.6(iv)$$

and:

$$\left(\frac{\partial^2 U_D}{\partial a^2}\right)_{a=a_0} = \frac{42}{a_0^2} U_{dd} + \frac{72}{a_0^2} U_{qd} \quad 2.6(v)$$

Using the exponential form for the repulsion energy:

$$\left(\frac{\partial^2 U_R}{\partial a^2}\right)_{a=a_0} = \frac{r_0^2}{a_0^2 p^2} \quad 2.6(vi)$$

this implies:

$$\frac{r_0^2}{p^2} U_R = 2U_{elec} - 2K \left(\frac{\partial H_0}{\partial a}\right)_{a=a_0} + K a_0 \left(\frac{\partial^2 H_0}{\partial a^2}\right)_{a=a_0} + 42U_{dd} + 72U_{qd} + \frac{9K}{\beta} \quad 2.6(vii)$$

and combining this with Equation 2.5(xviii) gives:

$$\frac{p}{r_0} = \frac{U_{elec} + 6U_{dd} + 8U_{qd} - K \left(\frac{\partial H_0}{\partial a}\right)_{a=a_0}}{2U_{elec} - 2K \left(\frac{\partial H_0}{\partial a}\right)_{a=a_0} + K a_0 \left(\frac{\partial^2 H_0}{\partial a^2}\right)_{a=a_0} + 42U_{dd} + 72U_{qd} + \frac{9K}{\beta}} \quad 2.6(viii)$$

which is the general form (after consideration of the point made previously) of the equation obtained by Jenkins and Waddington (1975a) and Jenkins (1976a). The omission of the possibility of the presence of complex ions leads

Theory

to the formula developed by Ladd and Lee (1958):

$$\frac{P}{r_0} = \frac{U_{\text{ELEC}} + 6 U_{\text{dd}} + 8 U_{\text{qd}}}{2 U_{\text{ELEC}} + 42 U_{\text{dd}} + 72 U_{\text{qd}} + (9 V_0 / \beta)} \quad 2.6(\text{ix})$$

Both Equations 2.6(viii) and 2.6(ix) have their denominators (especially) dominated by the dispersion energies and a large term involving the compressibility. As has already been pointed out in Section 2.4 the values calculated for dispersion energies can be unreliable. Compressibilities also are often subject to large uncertainties. Such features make the use of these equations undesirable until better methods are found for the calculation of dispersion energies and the quantification of ionic compressibilities. Their use must also be restricted to cubic cases.

For the reasons stated above the method described in the next section has not yet been extended to include second derivative calculations.

## 2.7 New General Method

The basis of the new method is to apply the principle of lattice energy maximisation (discussed in Section 2.5)

### Theory

in a general sense to the most rigorous and viable method of lattice energy calculation available. Such an approach maximises the information obtained from the input data and in turn promises more reliable results for lattice energies. As yet maximisation has only been applied with respect to the unit cell lengths because of the complications introduced by the necessity of considering complex ions as rigid bodies. The method is outlined in Jenkins and Pratt (1978b).

The method does not aim to produce simple equations like those obtained in Section 2.5 but rather is interceded for implementation within a computer package. A process described in Section 3. Each energy term in the term-by-term approach is calculated by the methods adopted in Sections 2.2-2.4.

The method will be parameterised here for a general triclinic lattice, a similar approach follows for all other symmetries.

The rigidity of complex ions in the lattice means that all internal distances of an ion must remain invariant on changes in the cell constants. This means it is necessary to split the fractional coordinates of an

atomic centre in a lattice into two parts, one part of which is allowed to vary with the cell lengths and one part which must remain constant. By choosing one atomic centre in an ion as 'basic' and defining all the atoms in the ion by the 'basic' coordinates plus a set of coordinates 'relative' to these we can achieve this split. Any movement of the 'basic' atomic centre moves the whole ion in a way as to retain its exact geometry if the 'relative' coordinates are maintained as constant. The 'basic' coordinates are designated  $(x_1, y_1, z_1)$  and the 'relative'  $(d_{x1}/a, d_{y1}/b, d_{z1}/c)$ , where the d's are the resolved parts of the fixed distance along the three cell axes. The general expression for the distance between atomic centres i and j in a triclinic system, having unit cell lengths a, b and c and angles  $\alpha$ ,  $\beta$  and  $\gamma$  is:

$$R_{ij} = (X^2 + Y^2 + Z^2 + 2XY\cos\gamma + 2YZ\cos\alpha + 2ZX\cos\beta)^{\frac{1}{2}} \quad 2.7(i)$$

where:

$$X = (x_j - x_1)a + d_{xj} - d_{x1} \quad 2.7(ii)$$

$$Y = (y_j - y_1)b + d_{yj} - d_{y1} \quad 2.7(iii)$$

# Theory

and:

$$Z = (z_j - z_i) c + d_{zj} - d_{zi} \quad 2.7(iv)$$

We now consider the calculation of the derivatives with respect to the cell lengths of the energy terms.

The electrostatic energy is composed of the Madelung energy of the lattice and the self energy of the complex ions. The self energy of the complex ions is given by Equation 2.2(viii), in which the only possible cell parameter dependence is in the interatomic distances. These distances are by their very nature inside complex ions and hence must be cell length independent, this is shown by the above equations where  $x_j = x_i$ , etc.. So the derivative of the self energy of the complex ions with respect to the cell lengths is zero and we can say (after Equation 2.2(v)):

$$\left( \frac{\partial U_{ELEC}}{\partial d} \right)_{d=d_0} = K \left( \frac{\partial M_1}{\partial d} \right)_{d=d_0} \quad 2.7(v)$$

where  $i$  is a, b or c and  $d_0$  is the equilibrium value. The subscript  $d$  again means that the geometries of

Theory

complex ions are assumed rigid.

The Bertaut method of calculating Madelung constants produces an equation:

$$M_1 = \frac{q}{RN} \sum_{i=1}^N n_i q_i^2 - \frac{1}{2\pi VN} \sum'_{h,k,l} \frac{|F_{hkl}|^2 \phi_{hkl}}{S_{hkl}^2} \quad 2.7(vi)$$

where  $q$  is a constant which depends on the charge density function used (for values see Waddington (1959)),  $R$  is the cut-off radius of the charge density function (see Equation 2.2(vi)),  $F_{hkl}$  is the Coulombic structure factor,  $\phi_{hkl}$  is the Fourier transform of the charge density function,  $S_{hkl}$  is the reciprocal lattice vector and  $(h,k,l)$  is a reciprocal lattice point. The second summation is over all positive and negative integer values of  $h$ ,  $k$  and  $l$  excluding the case when  $h=k=l=0$ .

The first term of Equation 2.7(vi) is cell length independent. The derivatives of the second term can be found if the derivatives of its four cell length dependent parts are known. They will be treated individually. The unit cell volume,  $V$ , is given by:

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma)^{\frac{1}{2}} \quad 2.7(vii)$$



and so the first derivative with respect to a unit cell length is immediately obtainable.

The reciprocal lattice vector is obtained from:

$$S_{hkl}^2 = \frac{1}{V^2} [h^2 b^2 c^2 \sin^2 \alpha + k^2 c^2 a^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma + 2hklabc^2 (\cos \alpha \cos \beta - \cos \gamma) + 2kla^2bc (\cos \beta \cos \gamma - \cos \alpha) + 2lhab^2c (\cos \gamma \cos \alpha - \cos \beta)] \quad 2.7(viii)$$

and so derivatives of this term are readily obtainable once the corresponding derivatives of the unit cell volume are known.

The Fourier transforms of the commonly used charge density functions are quoted by Templeton<sup>and Jones</sup> (1956). In this laboratory the parabolic form is generally used, such that (see Section 2.2):

$$\sigma_2(r) = \frac{15 (R - r)^2}{2\pi R^5} \quad 2.7(ix)$$

whereupon  $q$  is  $25/38$  and:

$$\phi_{hkl} = \frac{60(\theta \cos \theta - 3 \sin \theta + 2\theta)}{\theta^5} \quad 2.7(x)$$

where:

$$\theta = 2\pi R s_{hkl} \quad 2.7(xi)$$

and the derivatives are easily obtained. Other charge density functions can be treated similarly, apart from the Gaussian case where problems are encountered when attempting to differentiate the overlap energy correction, a term which is not necessary for simpler functions.

The argument of the Coulombic structure factor is given by:

$$|F_{hkl}|^2 = \left[ \sum_{i=1}^n q_i \sum_{j=1}^{n_i} \cos A_{ij} \right]^2 + \left[ \sum_{i=1}^n q_i \sum_{j=1}^{n_i} \sin A_{ij} \right]^2 \quad 2.7(xii)$$

where:

$$A_{ij} = 2\pi \left[ h(x_{ij} + d_{xij}/a) + k(y_{ij} + d_{yij}/b) + l(z_{ij} + d_{zij}/c) \right] \quad 2.7(xiii)$$

Again the derivatives with respect to unit cell lengths are readily obtained, consequently the derivatives

Theory

of the electrostatic energy can be obtained. The above approach is made the basis for a computer program (Jenkins and Pratt (1973a)) to calculate the electrostatic energy and its derivatives for a compound. The structure of the program is similar to the subroutine UELEC described in Section 3.

Inspection of Equations 2.3(v), 2.4(viii) and 2.4(ix) shows that the repulsion energy and the two terms contributing to the dispersion energy have a similar format which can be represented by:

$$U_T = \frac{1}{2N} \sum_{i=1}^N \sum_{j=1}^N t_{ij} \sum_{k=1}^{n_i} \sum_{l=1}^{n_j} f_T(R_{kl}) \quad 2.7(xiv)$$

where the terms  $t_{ij}$  are independent of the cell lengths (in fact of the crystal structure) and are given along with the function  $f_T$  in Table 2.7(i). Consequently we can say:

$$\left( \frac{\partial U}{\partial l_i} \right)_{l_i=l_{i0}} = \frac{1}{2N} \sum_{i=1}^N \sum_{j=1}^N t_{ij} \sum_{k=1}^{n_i} \sum_{l=1}^{n_j} \frac{df_T(R_{kl})}{dR_{kl}} \cdot \left( \frac{\partial R_{kl}}{\partial l_i} \right)_{l_i=l_{i0}} \quad 2.7(xv)$$

The first derivative appearing on the right hand side of the above equation (that of the function with respect

Table 2.7(i) Amplification of the general terms of  
Equation 2.7(xiv).

	$r_{ij}$	$f_T(r_{kl})$	Reference
$r$	$r_{ij} \exp\left(\frac{\bar{r}_i + \bar{r}_j}{e}\right)$	$\exp(-r_{kl}/e)$	Equations 2.3(iv) and 2.3(v)
$u$	$r_{ij}$	$(r_{kl})^{-6}$	Equations 2.4(viii) and 2.4(x)
$u$	$r_{ij}$	$(r_{kl})^{-8}$	Equations 2.4(ix) and 2.4(xi)

to the distance) is simply obtained by inspecting the form of the function  $f_T$ . The derivatives of the distance with respect to the cell lengths are obtained by operation on Equation 2.7(i).

One can obtain the summations of the derivative terms in an exactly analogous way to the summations in Equation 2.7(xiv), by direct summation over the lattice. A computer program (similar to the subroutine SUMS - see Section 3) has been written for this purpose. The convergence of the derivative summations is very similar to that of the simple summations which is discussed in Sections 2.3 and 2.4.

We are now in a position to feed the derivatives obtained by the methods described above into equations of the form of Equation 2.5(ii). Up to three different equations of this type, depending on the lattice symmetry, can be produced for each full crystal structure.

Normally in these equations the dispersion energy and its derivative(s) are known (as well as is possible anyway) and are simple figures. Often the electrostatic energy and derivatives are known only as functions (quadratics) of charge distributions in complex ions and

the repulsion energy and derivatives as functions of unknown basic radii. Generally we can write in this case up to three equations of the form:

$$\sum_{i=1}^N \sum_{j=1}^N \Theta_{ij} \exp\left(\frac{r_{ij}}{\rho}\right) = \Omega \quad 2.7(xvi)$$

where both  $\Theta_{ij}$  and  $\Omega$  can be functions of the unknown charges;  $\Omega$  a quadratic and  $\Theta_{ij}$  linear (as a consequence of the  $c_{ij}$  terms (see Table 2.7(i))).

The normal situation, the one mainly considered here, is when only one basic radius is unknown and only one charge is independently varied. If only one type of complex ion is present in the lattice and it is composed of two different types of atom (this covers most common inorganic ions) then the charge distribution in the complex ion may be described in terms of one variable parameter. To fulfill the other condition one has to choose a model for the calculation of the repulsion energy (see Section 2.8) which contains only one unknown basic radius. In this case Equation 2.7(xvi) reduces to:

$$\sum_{i=0}^2 \Theta_i \exp\left(\frac{i \cdot r}{\rho}\right) = \sum_{i=0}^2 \Omega_i q_i \quad 2.7(xvii)$$

where  $\bar{r}_x$  is the unknown basic radius and it must be remembered that the  $\theta_i$ 's may still be linear functions of the unknown charge  $q_Y$ .

We now have up to three relationships between two unknown quantities, so we can either obtain 'best' values for them (if we have more than one relationship) or for each value of the charge we can assign value(s) of  $\bar{r}_x$  and hence value(s) for the lattice energy, using this or related thermochemical properties to obtain the 'true' value for  $q_Y$ .

The application of this general method will be clarified in the results section in the study of actual cases.

## 2.6 Parameter Dependence

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The major objective of the method described in the previous section is the calculation of reliable values for the lattice energies of ionic crystals. The reliability of the values produced can be judged by the determination of the dependence of lattice energies on the parameters used in their calculation. It must be stressed that the large reduction in dependence produced by the energy

minimisation does not imply an insensitive method or that parameter choice is unimportant. The better the choice of parameters still means a better (i.e. more accurate) lattice energy, but in cases where any parameters are not known at all the method can still sometimes be used to give an estimate of the lattice energy. The minimisation provides a mechanism for the reduction of possible errors.

Obviously there will be differences in variation from one compound to another but it is felt that the general features found for one compound should be sufficient to give an adequate illustration. Potassium hexafluorogermanate ( $K_2GeF_6$ ) has been chosen as the illustrative salt for the following reasons:

- (a) it contains a complex ion (the hexafluorogermanate ion,  $GeF_6^{2-}$ );
- (b) its crystal structure has trigonal symmetry and, when hexagonal axes are used, has two different cell lengths. Such symmetry gives two curves for the lattice energy as a function of the charge distribution which define a unique solution on intersection;
- (c) the crystal structure is reasonably simple (unimolecular) and hence aids repetitive calculations, in that it minimises the computer time required;

#### Theory



(d) the salt was already under consideration as part of the extended study on  $A_2MX_6$  salts included in the research programme.

The assumption has to be made in these calculations (and all others discussed here) that not only  $\rho$ , the repulsion exponent, but also the basic radii are isotropic. This means that a perfectly spherical charge distribution is assumed for all atoms. In salts like potassium hexafluorogermanate this seems reasonable but where interacting atoms have large differences in polarisabilities (for instance in a lithium analogue) deviations from the isotropic approximation can be expected.

The crystal structure of potassium hexafluorogermanate (Wyckoff (1955)) has trigonal symmetry and belongs to the space group  $P\bar{3}m1$ . It is convenient here to express the structure with hexagonal axes (trigonal axes give only one relationship of the type of Equation 2.7(xvii) whilst hexagonal axes give two). The equilibrium cell lengths are  $a_0 = 5.62\text{\AA}$  and  $c_0 = 4.65\text{\AA}$  and using the notation of the 'International Tables for X-ray Crystallography' the atomic coordinates are:

$$K = (2d) = \frac{1}{3}(1/3, 2/3, z) \text{ with } z = 0.70$$

Theory

$$\text{Ge} - (1a) - (0,0,0)$$

$$\text{F} - (6i) - \frac{1}{2}(x, \bar{x}, z; x, 2x, z; 2\bar{x}, \bar{x}, z) \text{ with } x=0.148, z=0.22$$

Before the development of the method discussed in Section 2.7 the best possible approach to the calculation of the lattice energy of potassium hexafluorogermanate would be similar to that adopted by Jenkins and Smith (1976) for the rubidium salts of the hexachlorostannate (IV) and hexachlorotellurate(IV) ions. The electrostatic energy would be calculated as a function of the charge distribution of the complex ion, specifically as a quadratic of the charge on the fluorine atoms ( $q_F$ ), where the residual charge on the germanium atom ( $q_{Ge}$ ) is given by:

$$q_{Ge} + 6 q_F = -2 \quad 2.8(1)$$

The dispersion energy would be calculated by taking a model for the hexafluorogermanate ion of six fluoride ions at the position of the fluorine atoms, and the repulsion energy by use of the same model with basic radii taken from work on the alkali halides (the repulsion exponent would be taken as 0.345<sup>9</sup> from Born and Mayer's (1932) results for the alkali halides). In order to obtain a

value for the lattice energy some estimate would have to be made of the charge distribution in the complex ion. Any error in this estimate would produce errors in the lattice energy (see later).

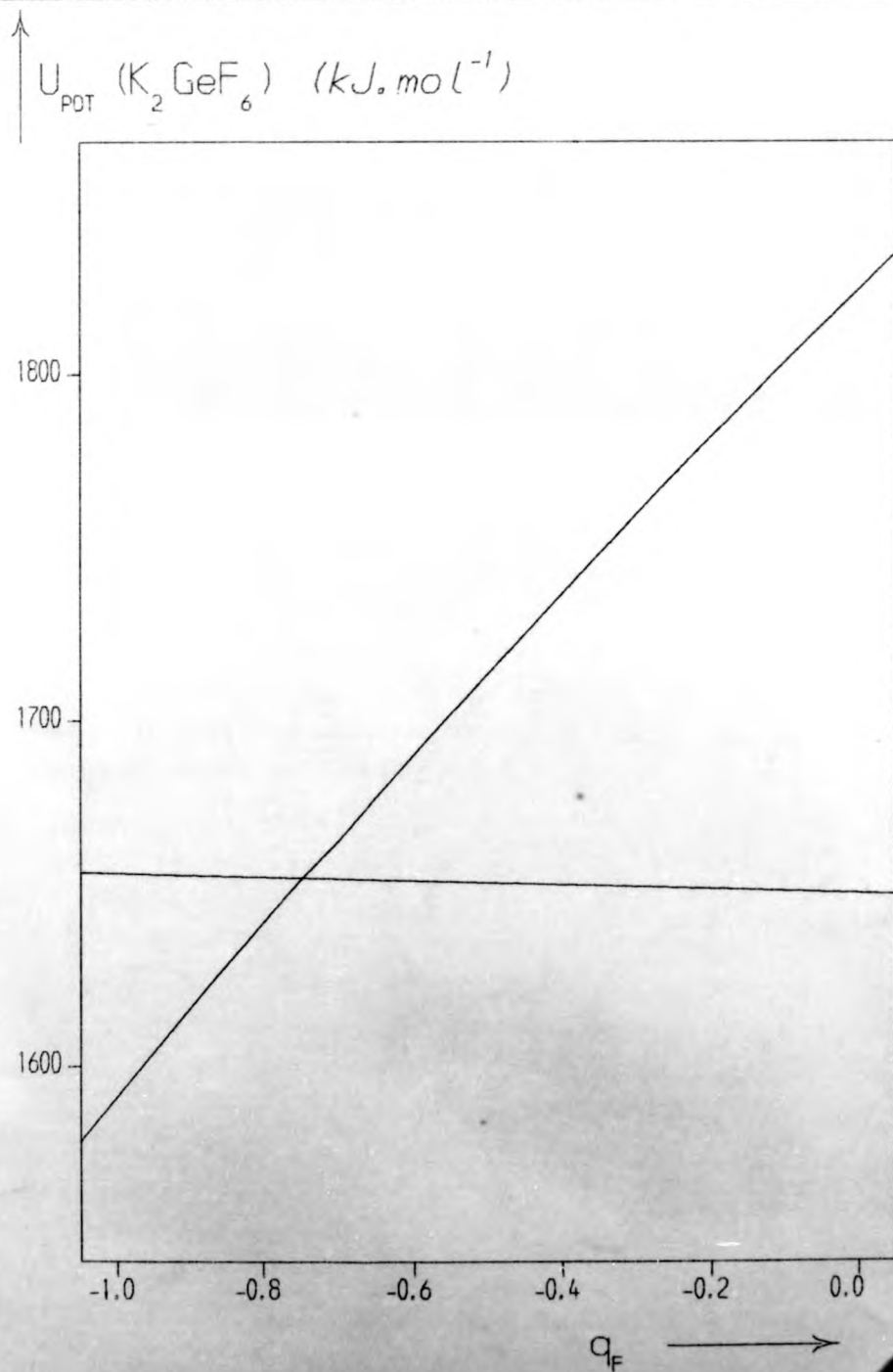
Application of the newly proposed method involves the calculation of the electrostatic and dispersion energies (also their associated derivatives with respect to cell lengths) by the same approach as the old method. However the models that can be adopted for the calculation of the repulsion energy (see later) are now much more flexible as in the method one basic radius can be held as variable. The repulsion model adopted in this section is that of six identical spheres at the position of the fluorine atoms. Two equations of the form of Equation 2.7(xvii) can be calculated. So each value of  $q_F$  assigns two values for the basic radius of the fluorine atom and hence two values for the lattice energy of potassium hexafluorogermanate. A plot of lattice energy versus  $q_F$  for this salt using this method is given in Figure 2.8(i). It is felt worthwhile to give complete numerical results for the method in this one case as an illustration. The calculations on potassium hexafluorogermanate give:

$$U_M = 1856.1 + 9536.0q_F + 20417.2q_F^2 \text{ kJ.mol}^{-1} \quad 2.8(ii)$$

$$U_{SE} = -9435.4q_F - 20454.9q_F^2 \text{ kJ.mol}^{-1} \quad 2.8(iii)$$

Theory

Figure 2.8(i) Lattice energy of potassium hexafluorogermanate.



$$\begin{aligned}
 U_{\text{ELEC}} &= 1856.1 + 100.6q_F - 37.7q_F^2 \text{ kJ.mol}^{-1} \quad 2.8(\text{iv}) \\
 \left(\frac{\partial U_{\text{ELEC}}}{\partial a}\right)_{a=a_0} &= -300.8 - 134.5q_F + 47.6q_F^2 \text{ kJ.mol}^{-1} \cdot \text{\AA}^{-1} \quad 2.8(\text{v}) \\
 \left(\frac{\partial U_{\text{ELEC}}}{\partial c}\right)_{c=c_0} &= -35.6 + 80.5q_F + 3.3q_F^2 \text{ kJ.mol}^{-1} \cdot \text{\AA}^{-1} \quad 2.8(\text{vi})
 \end{aligned}$$

where the derivative with respect to  $a$  assumes an isotropic situation.

The results for the dispersion energy and derivatives are given in Table 2.8(i), the parameters used in their calculation are discussed in the section on hexahalometallate salts. The repulsion energy and derivatives can be expressed by (using the six fluorine atom model):

$$\begin{aligned}
 U_R &= 5.58c_{\text{KK}} + 10.74c_{\text{KF}} \exp(\bar{r}_F/\rho) + \\
 &\quad 6.116c_{\text{FF}} \exp(2\bar{r}_F/\rho) \text{ kJ.mol}^{-1} \quad 2.8(\text{vii}) \\
 \left(\frac{\partial U_R}{\partial a}\right)_{a=a_0} &= -6.15c_{\text{KK}} - 13.28c_{\text{KF}} \exp(\bar{r}_F/\rho) - \\
 &\quad 6.136c_{\text{FF}} \exp(2\bar{r}_F/\rho) \text{ kJ.mol}^{-1} \cdot \text{\AA}^{-1} \quad 2.8(\text{viii}) \\
 \left(\frac{\partial U_R}{\partial c}\right)_{c=c_0} &= -3.36c_{\text{KK}} - 6.41c_{\text{KF}} \exp(\bar{r}_F/\rho) - \\
 &\quad 6.174c_{\text{FF}} \exp(2\bar{r}_F/\rho) \text{ kJ.mol}^{-1} \cdot \text{\AA}^{-1} \quad 2.8(\text{ix})
 \end{aligned}$$

where  $c_{\text{KK}}=1.25$ ,  $c_{\text{KF}}=1.125+0.125q_F$ ,  $c_{\text{FF}}=1.0+0.25q_F$ ,  $\bar{r}_F$  is the (variable) radius of the fluorine atoms in this model,  $\rho$  is taken as  $0.345 \text{\AA}$  and the basic radius of the potassium ion is taken as  $1.19 \text{\AA}$  (Jenkins and Pratt

Table 2.8(i) Dispersion energy, and cell length derivatives, for potassium hexafluorogermanate.

Term	'K-K'	'K-F'	'F-F'	Total	Units
$U_{dd}$	4.9	62.4	22.2	89.5	$\text{kJ. mol}^{-1}$
$\left(\frac{\partial U_{dd}}{\partial a}\right)_{a=a_0}$	-3.5	-55.6	-17.7	-76.8	$\text{kJ. mol}^{-1} \cdot \text{\AA}^{-1}$
$\left(\frac{\partial U_{dd}}{\partial c}\right)_{c=c_0}$	-2.2	-26.5	-17.4	-46.2	$\text{kJ. mol}^{-1} \cdot \text{\AA}^{-1}$
$U_{qd}$	0.3	5.5	1.0	7.0	$\text{kJ. mol}^{-1}$
$\left(\frac{\partial U_{qd}}{\partial a}\right)_{a=a_0}$	-0.3	-7.1	-1.0	-8.4	$\text{kJ. mol}^{-1} \cdot \text{\AA}^{-1}$
$\left(\frac{\partial U_{qd}}{\partial c}\right)_{c=c_0}$	-0.2	-3.3	-1.2	-4.6	$\text{kJ. mol}^{-1} \cdot \text{\AA}^{-1}$

(1977a)).

The intersection point of Figure 2.8(i) gives the following values:

$$q_F = -0.75 \quad 2.8(x)$$

$$\bar{r}_F = 0.948 \text{ \AA} \quad 2.8(xi)$$

$$U_{\text{ELEC}} = 1759.8 \text{ kJ.mol}^{-1} \quad 2.8(xii)$$

$$U_R = 5.6 + 173.2 + 23.1 = 201.9 \text{ kJ.mol}^{-1} \quad 2.8(xiii)$$

$$U_{\text{POT}} = 1654.5 \text{ kJ.mol}^{-1} \quad 2.8(xiv)$$

The three separate terms for the repulsion energy correspond to the contributions from potassium-potassium, potassium-fluorine and fluorine-fluorine repulsions respectively.

So the calculation of the lattice energy is possible without requiring any parameters external to the method (this situation could not be reached by the old method). Also a more flexible model for the repulsion energy has been used.

The object of this section is to compare the parameter dependence of the new method with the direct dependence shown by the old method; illustrating the fact that the energy minimisation greatly reduces the parameter

dependence. The earlier method cannot be applied directly for the reasons stated earlier and it is necessary to use the results for the charge distribution and basic radius given in Equations 2.8(x) and 2.8(xi). Such a procedure would produce equivalence of the two methods if the initial choice of parameters were used.

The first parameter we consider is the charge on the fluorine atom. Inspecting the earlier results gives this relationship for the old method:

$$\frac{\partial U_{\text{TOT}}}{\partial q_F} = 100.6 - 75.5q_F - 1.34 \exp\left(\frac{\bar{r}_F}{\rho}\right) - 0.029 \exp\left(\frac{2\bar{r}_F}{\rho}\right) \text{ kJ.mol}^{-1} \quad 2.8(xv)$$

which at the point defined by Equations 2.8(x) and 2.8(xi) has the numerical value of  $129 \text{ kJ.mol}^{-1}$  (dominated by the terms arising from the electrostatic energy). This is fairly small here, but could be much larger in other compounds. As the new method determines the charge distribution by intersection no comparison can be made in this case. This possibility of variation in charge, although never by a great amount, is one of the mechanisms by which the minimisation reduces the parameter dependence.



One of the two major possible sources of error in lattice energy calculations is the dispersion energy. As the form of the equation used for its calculation is debatable (see Section 2.4) it is thought worthwhile investigating the dependence of replacing the dipole-dipole dispersion energy,  $U_{dd}$ , by  $U_{dd}^1$  where:

$$U_{dd}^1 = k_{dd} U_{dd} \quad 2.8(xvi)$$

Curves of  $U_{POT}$  versus  $k_{dd}$  for both the old (dotted line) and new (full line) methods are given in Figure 2.8(ii), the latter being a plot of values obtained from the intersection of the derivative curves. It is seen that the variation, over this range, is reduced by the new method to about 30% of that shown by the old method. It is reassuring to note that even if the dipole-dipole dispersion term was underestimated by a factor of two a possible increase in lattice energy of  $90 \text{ kJ.mol}^{-1}$  is kept down to less than  $30 \text{ kJ.mol}^{-1}$ .

A similar investigation of the dipole-quadrupole dispersion energy, involving a variable  $k_{qd}$ , is shown in Figure 2.8(iii). It shows a reduction in dependence to under 7% and so even large errors in this term are

Figure 2.8(ii) Example of lattice energy dependence on dipole-dipole dispersion energy.

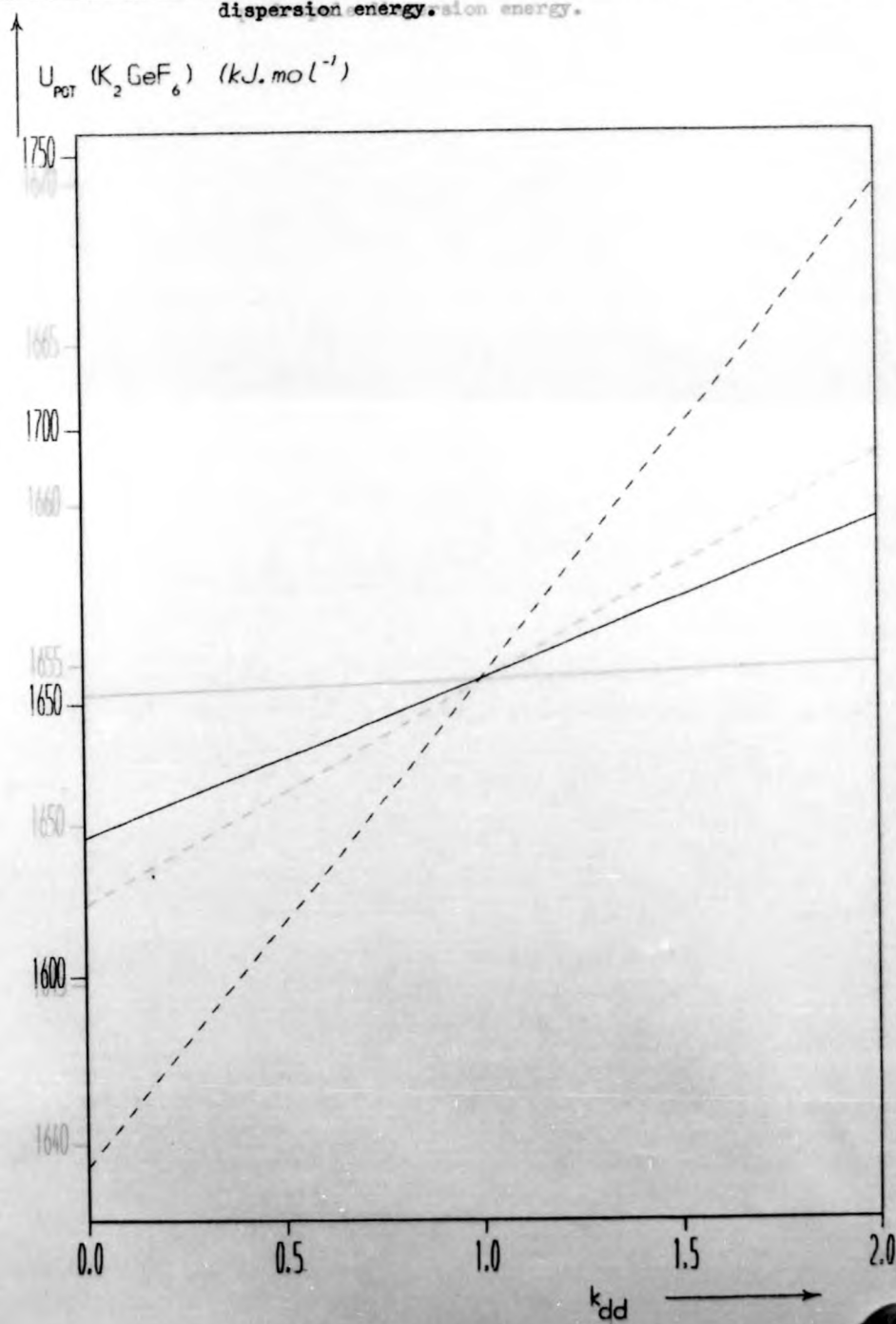


Figure 2.8(ii) Example of lattice energy dependence on dipole-dipole dispersion energy.

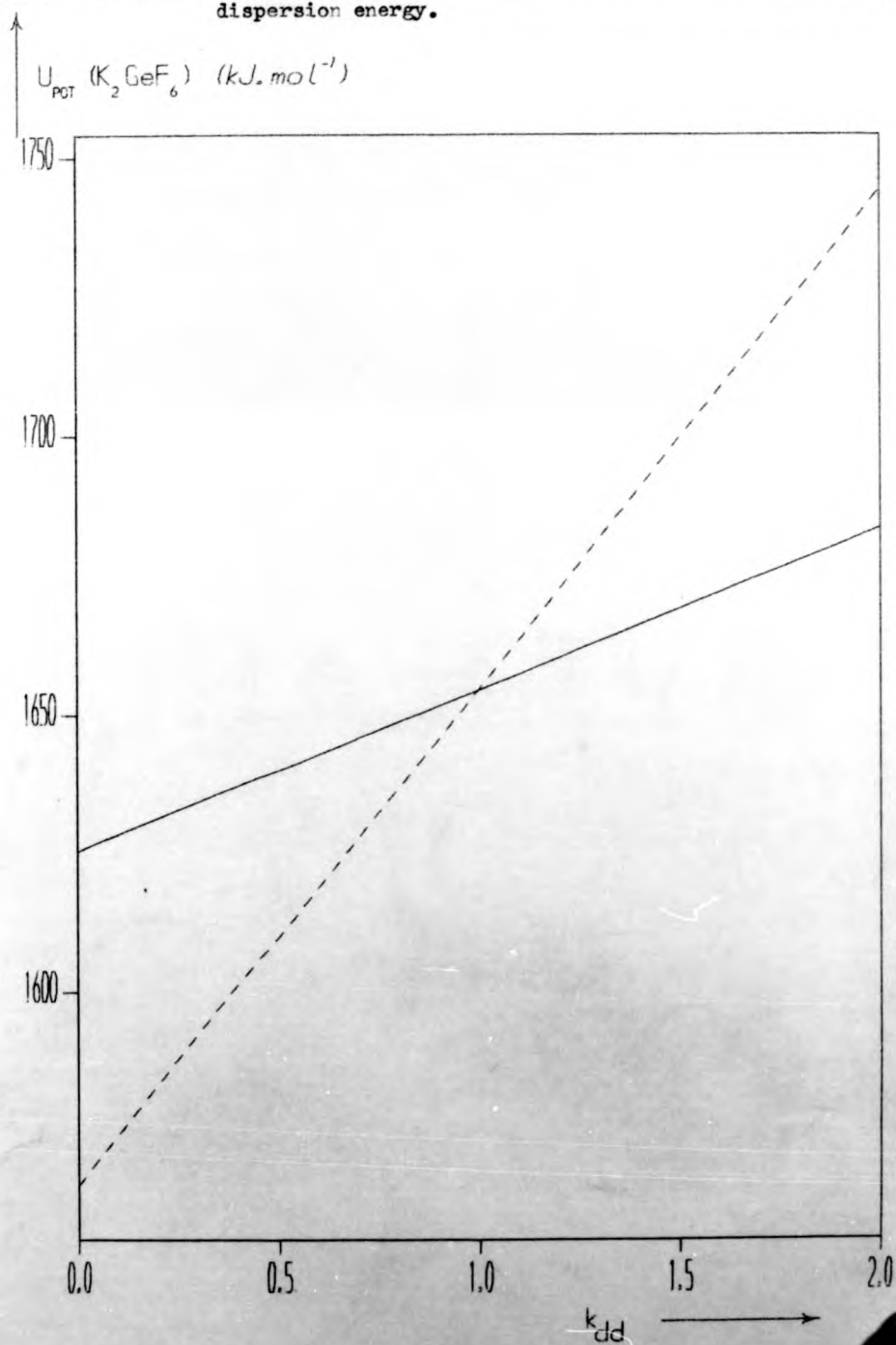
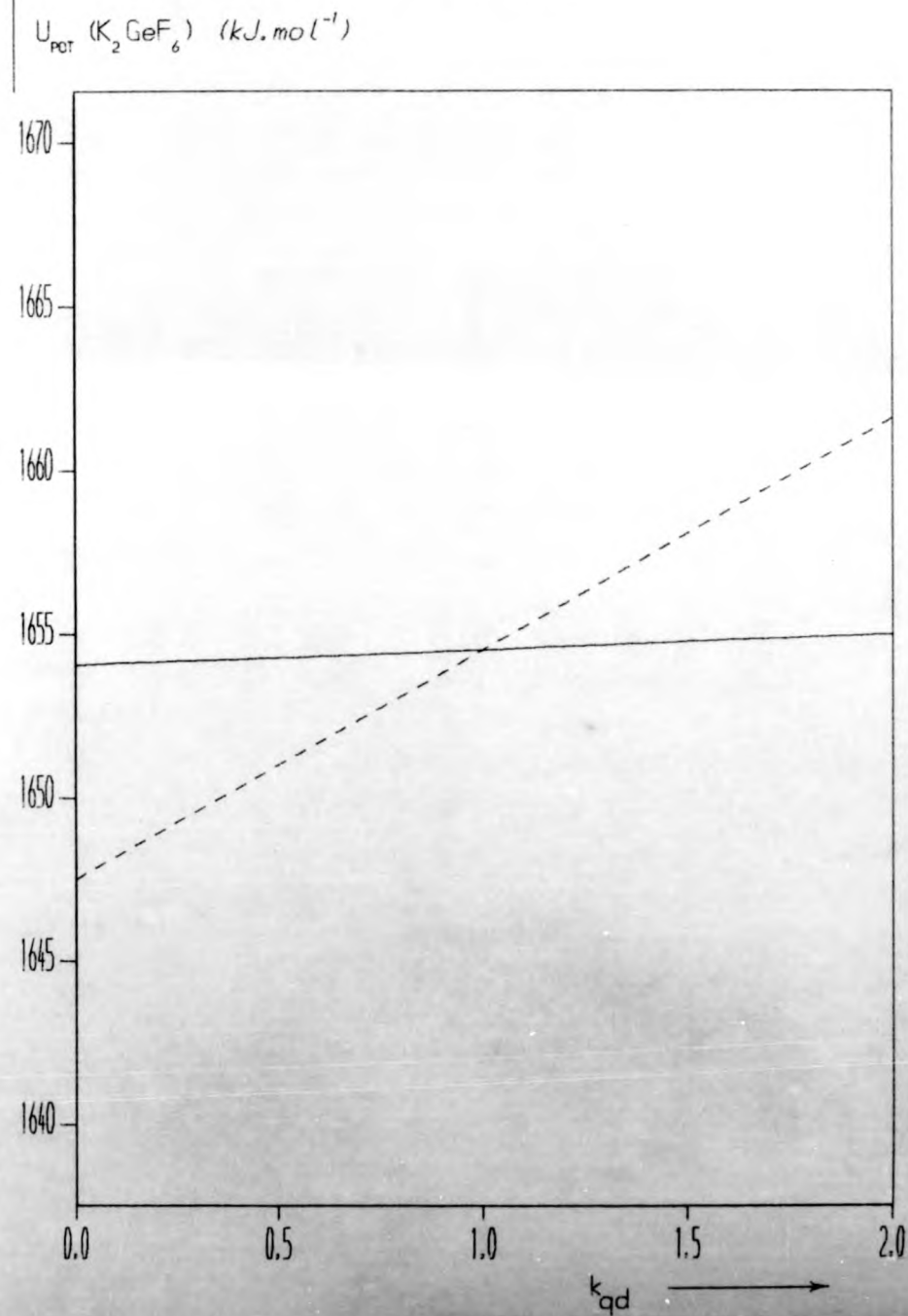


Figure 2.8(iii) Example of lattice energy dependence on dipole-quadrupole dispersion energy.



virtually eliminated by the minimisation.

If we now take the London formulae for the dispersion energy we can investigate the effect of the ion parameters used in these formulae (Equations 2.4(viii)-2.4(xii)). The fluorine atom (or ion as it is assumed in the dispersion model) contributes more to the dispersion energy than the potassium ion and so its parameters are used for the investigation. If we replace the polarisability of the fluorine ion,  $d_F$ , by  $d_F^i$  where:

$$d_F^i = k_d d_F \quad 2.8(xvii)$$

we can show the dependence on this parameter by a plot of lattice energy against  $k_d$  for the old (dotted line) and new (full line) methods (Figure 2.8(iv)). Again the minimisation reduces the dependence to about 30% of that which would be shown by direct substitution. Adopting a similar approach with the characteristic energy of the fluorine ion,  $E_F$ , with a parameter  $k_e$  we obtain Figure 2.8(v), which again shows the factor of 70% improvement in dependence. The variation with characteristic energy is small enough to make any errors associated with it reasonably unimportant.

#### Theory

Figure 2.8(iv) Example of lattice energy dependence on ion polarisability.

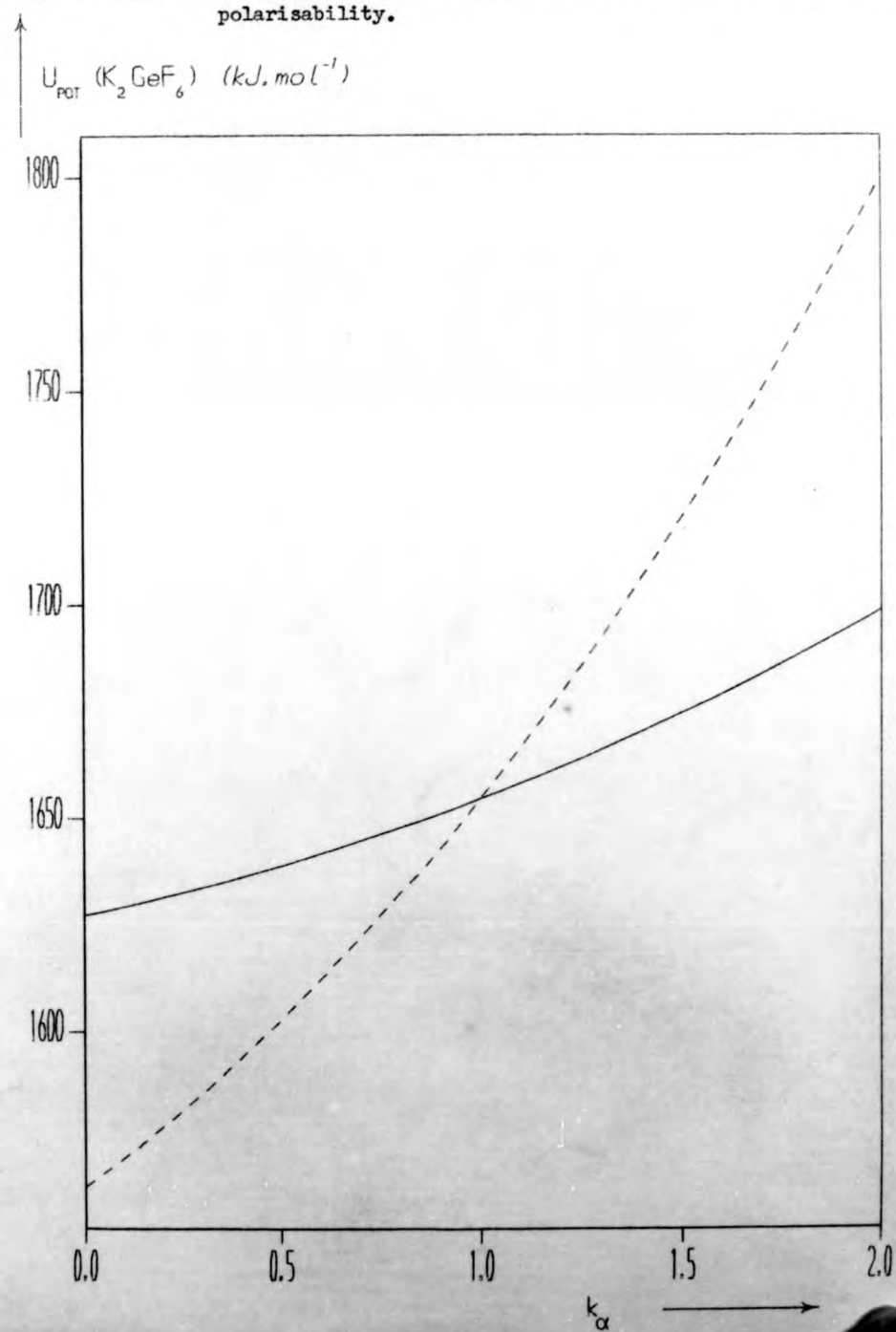


Figure 2.8(v) Example of lattice energy dependence on ion characteristic energy.

$U_{\text{POT}} (\text{K}_2\text{GeF}_6) (\text{kJ} \cdot \text{mol}^{-1})$

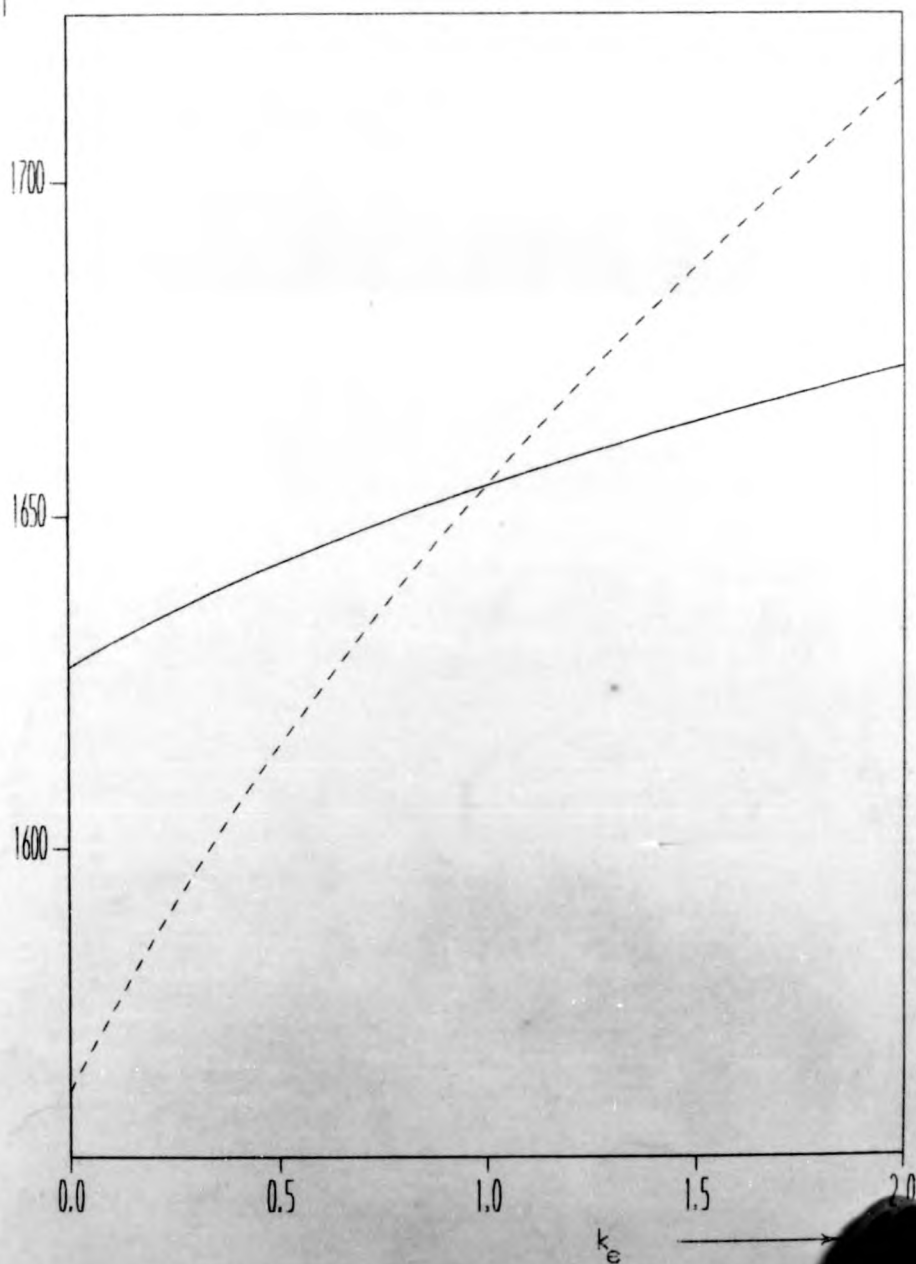
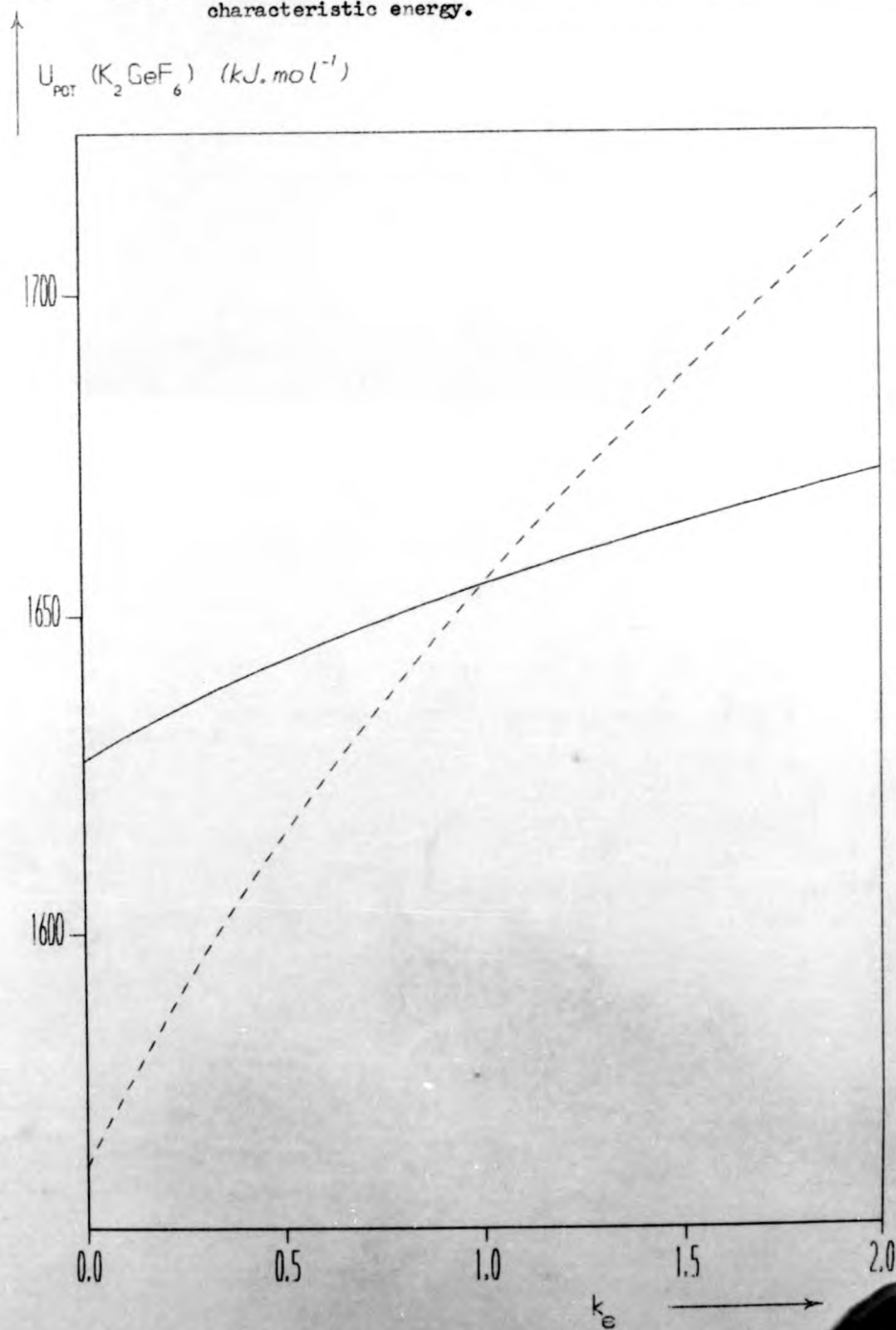




Figure 2.8(v) Example of lattice energy dependence on ion characteristic energy.





The electron number of the fluorine atom/ion,  $p_F$ , occurs not only in the dipole-quadrupole dispersion energy but also in the repulsion energy. Despite this, on replacement by  $p_F^i$  where:

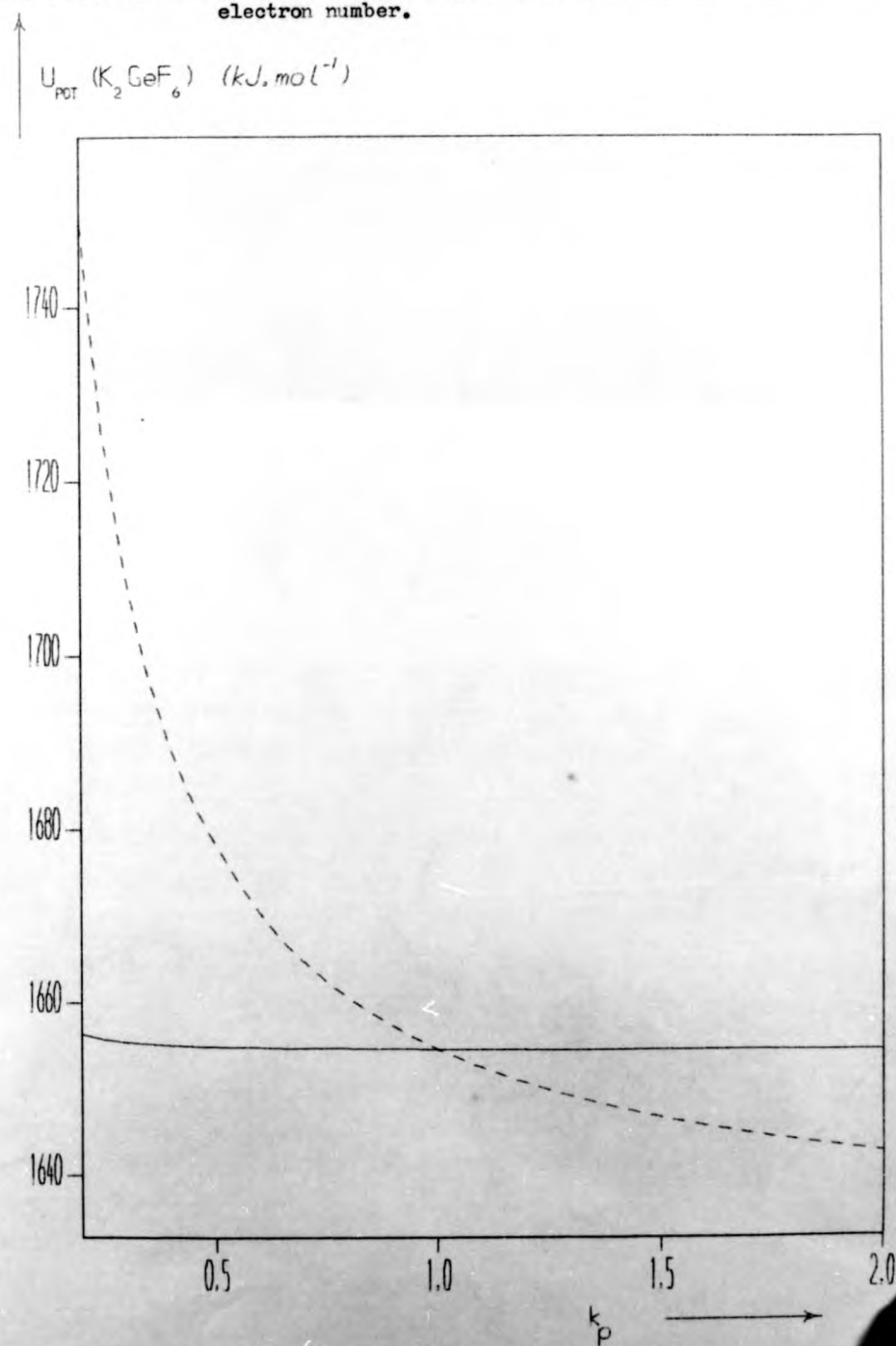
$$p_F^i = k_p p_F \quad 2.8(xviii)$$

it can be seen (Figure 2.8(vi)) that the minimisation reduces the effect of this parameter to virtually zero. Hence in this research the approximation of using the number of valence electrons is felt adequate.

In general we can say that possible errors in the dispersion energy will have only a small effect on the lattice energy calculated by the new method. Though it is important that more accurate methods should be developed for the calculation of this term it can be seen that the results currently obtained can still be considered to give reasonable accurate lattice energies without necessarily being very accurate themselves.

There are two possible variable parameters in the repulsion energy, aside from the charge distribution and electron number mentioned previously, namely the basic

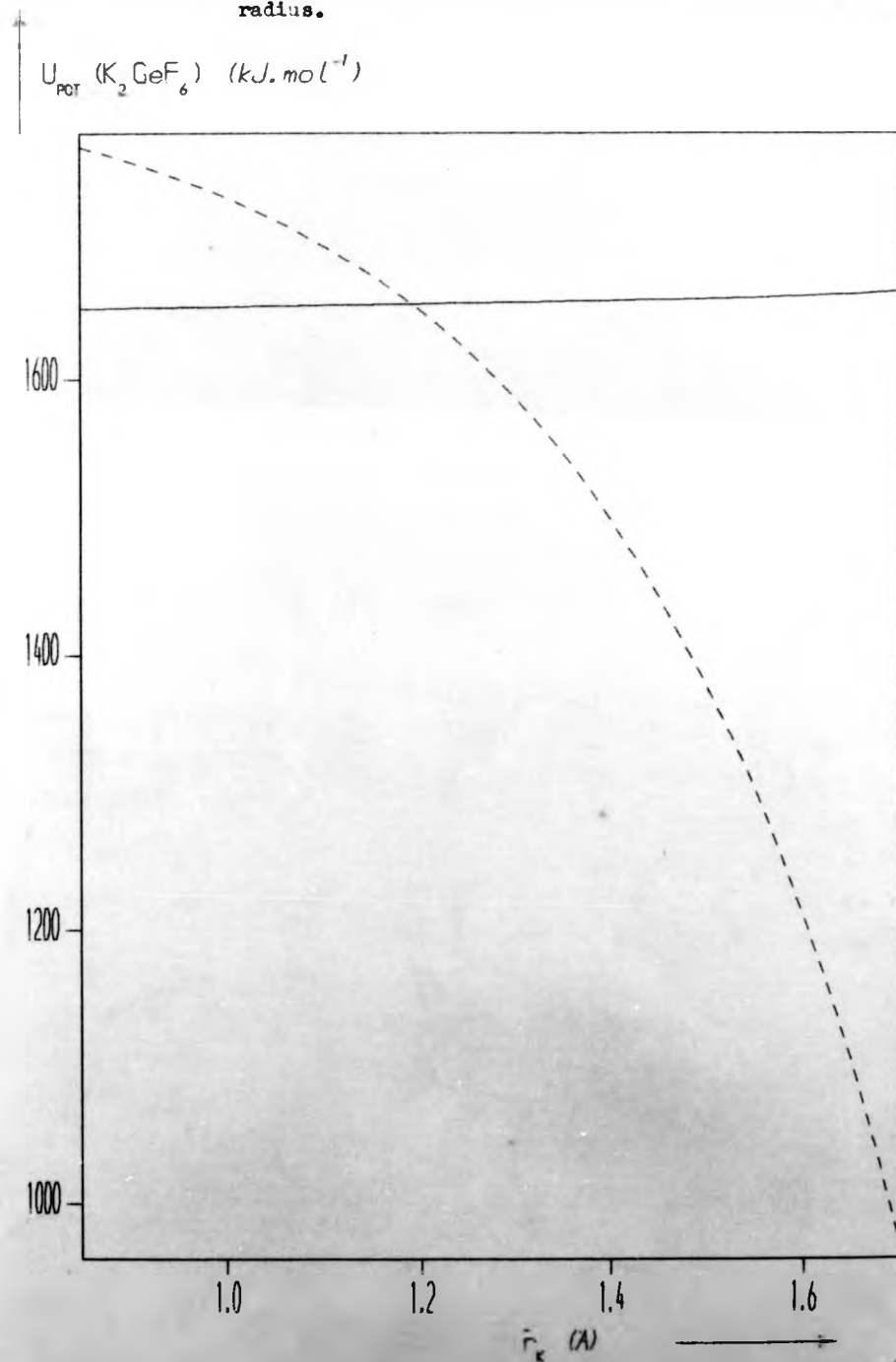
Figure 2.8(vi) Example of lattice energy dependence on ion electron number.



radius and the repulsion exponent. It is not possible to compare the dependence on the fluorine atom basic radius as it is calculated by the new method, but it is possible to investigate the dependence on the potassium ion basic radius. This dependence is shown in Figure 2.9(vii) for the old (dotted line) and new (full line) methods. The very large dependence shown by the old method is almost totally eliminated by the new method; the dependence is in fact reversed in direction over this range (about 1.52). So it is not necessary now to have very accurate basic radii as the other radius (and the charge) calculated virtually compensate the repulsion energy to give almost the same lattice energy irrespective of the values used.

The repulsion exponent is one of the most influential parameters in the potential, and it is also the most difficult to quantify for reasons discussed in Section 2.6. It is only for simple systems that values exist, 0.345<sup>8</sup> has been established for the alkali halides (Born and Mayer (1932)). In work on more complicated systems we have chosen to adopt this value as a constant and this is an assumption with little justification, although virtually unavoidable (the basic radii however provide variation in the repulsion exponents). It is very important then to estimate the effect of this assumption

Figure 2.8(vii) Example of lattice energy dependence on ionic radius.

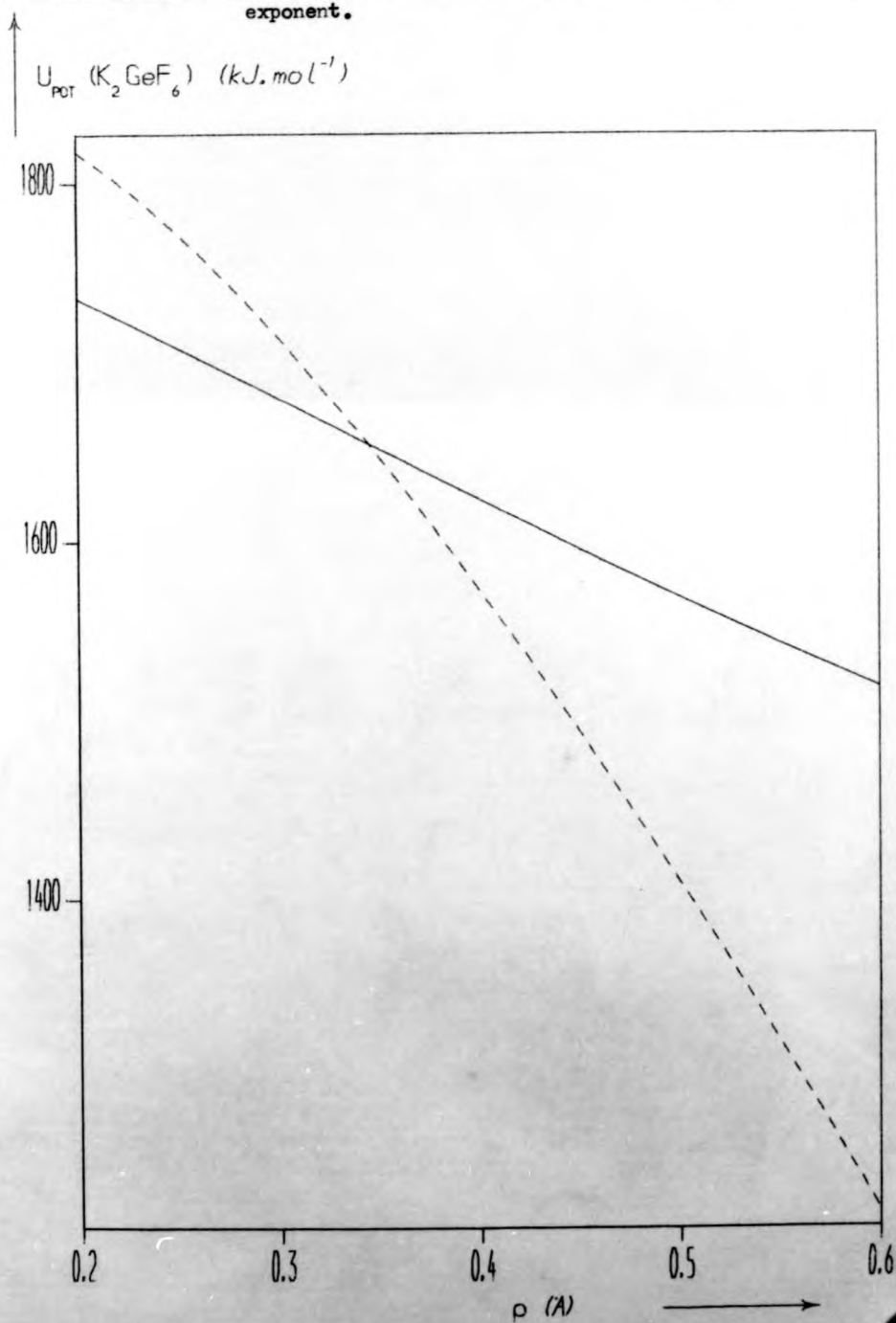


within the newly proposed method. In Figure 2.3(viii) the lattice energy of potassium hexafluorogermanate is plotted against the repulsion exponent,  $p$ , for the old (dotted line) and new (full line) methods. The range of  $p$  is 6.2-9.6 and all possible real situations should lie around mid-range. The dependence over the whole range is reduced in the new method to 36% of that shown by the old, and perhaps more importantly a variation either side of 8.345 now gives a range of lattice energy values of only  $\pm 12 \text{ kJ. mol}^{-1}$ . This variation is still not as low as one would hope but is a great improvement and means that lattice energies should invariably be reasonably accurate.

The choice of model for the dispersion energy calculation is usually forced by circumstances as there are a limited number of ions for which the polarisability and characteristic energy are known. There is certainly no reasonable alternative to the six fluoride ion model used here for the hexafluorogermanate ion and so no investigation of alternatives can be made.

The restriction on the choice of model for the calculation of the repulsion energy is that only one unknown size of sphere (i.e. one unknown basic radius) can be used if a solution is to be obtained. However, although

Figure 2.8(viii) Example of lattice energy dependence on repulsion exponent.



this restriction does not allow an exact repulsion envelope to be considered, a good approximation can invariably be selected. In the examples quoted here all the spheres are assumed to be centered on the atomic positions. The fluorine positions are depicted by the numerals 1 to 6; with the opposite pairs being 1 and 2, 3 and 4 and 5 and 6. The germanium position is depicted by the numeral 7. Six different models for the hexafluorogermanate ion have been considered (A-F), the intersection point results for these are given in Table 2.8(ii). Model A (the spherical union model) is clearly an unrealistic model as it would not be expected to be as good as E or F and it gives quite a different value for the lattice energy. The lower charge distribution shown by Model A can be explained by the larger surface over which this model would apparently distribute the total charge. Models B, C and D are clearly unrealistic as they omit atoms in a way so as to totally change the symmetry of the ion in question. They are included only for comparison and it can be seen that they are flexible enough for the minimisation to produce values close to those obtained by the more realistic models. Model E is the one used in the previous discussions, i.e. six spheres at the positions of the fluorine atoms. Model F appears more general than E however it includes the restriction that the basic radius

Table 2.8(ii) Results (by intersection) for the various repulsion models of the hexafluorogermanate ion.

Model	Atomic positions Included	$q_F$	Results	
			$\bar{r}$ (Å)	$U_{POT}$ (K <sub>2</sub> GeF <sub>6</sub> ) (kJ.mol <sup>-1</sup> )
A	7	-0.419	2.170	1682.1
B	1,2	-0.629	1.382	1656.9
C	1,2,7	-0.628	1.323	1659.0
D	3,4,5,6	-0.725	1.100	1655.0
E	1,2,3,4,5,6	-0.747	0.948	1645.5
F	1,2,3,4,5,6,7	-0.735	0.932	1655.5

Theory



of the central sphere must be the same as the outer spheres, and so it is not generally used. The closeness of the results obtained from models E and F encourages the belief that both are sufficiently close to the real envelope to be suitable for general use. Models A and E are depicted in a plan view of the hexafluorogermanate ion in Figure 2.8(ix) where an (intuitive) approximation to the real envelope is also shown. A close approach to the real envelope would be a linear combination of models A and F, of which F is an example.

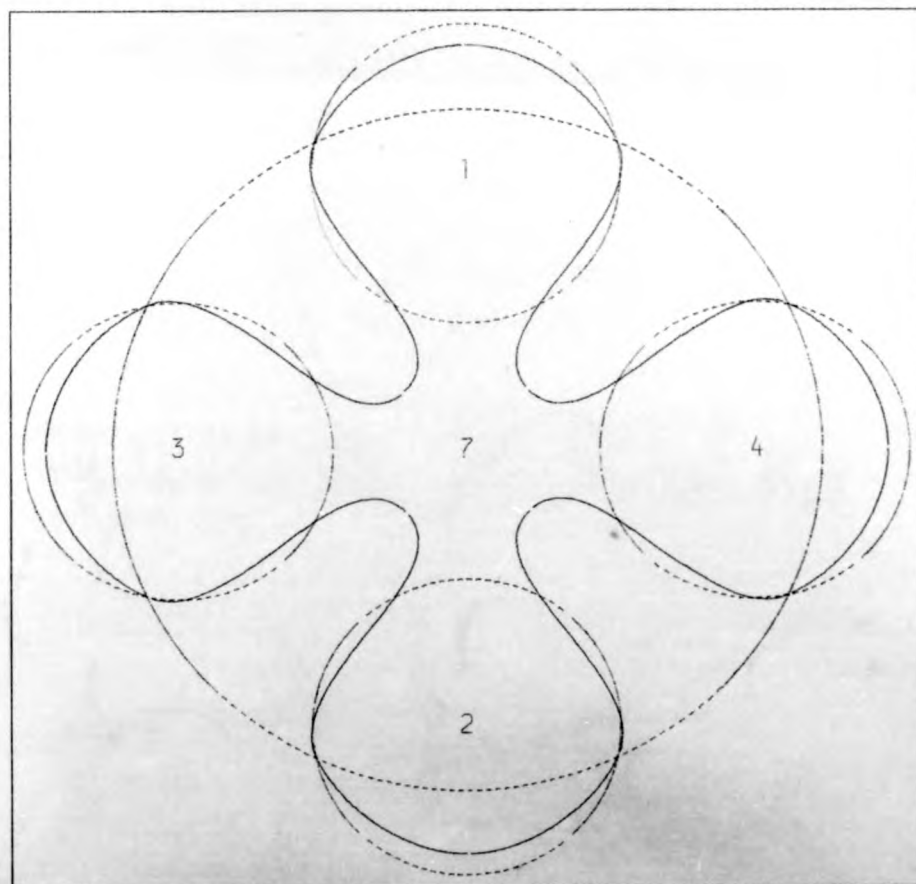
The major conclusion from Table 2.8(ii) must be that as long as a model is fairly realistic and 'flexible' (unlike model A) the minimisation will produce a good result for the lattice energy.

The new method provides another safeguard not present in the old. The solution of equations of the form of Equation 2.7(xvii) is an expression of the type:

$$F = p \ln \left[ \frac{-B \pm (B^2 - 4AC)^{1/2}}{2A} \right] \quad 2.8(xix)$$

where A, B and C are charge dependent. This means that solutions are limited to the cases when both the

Figure 2.8(ix) Repulsion envelopes for hexafluorogermanate ion.



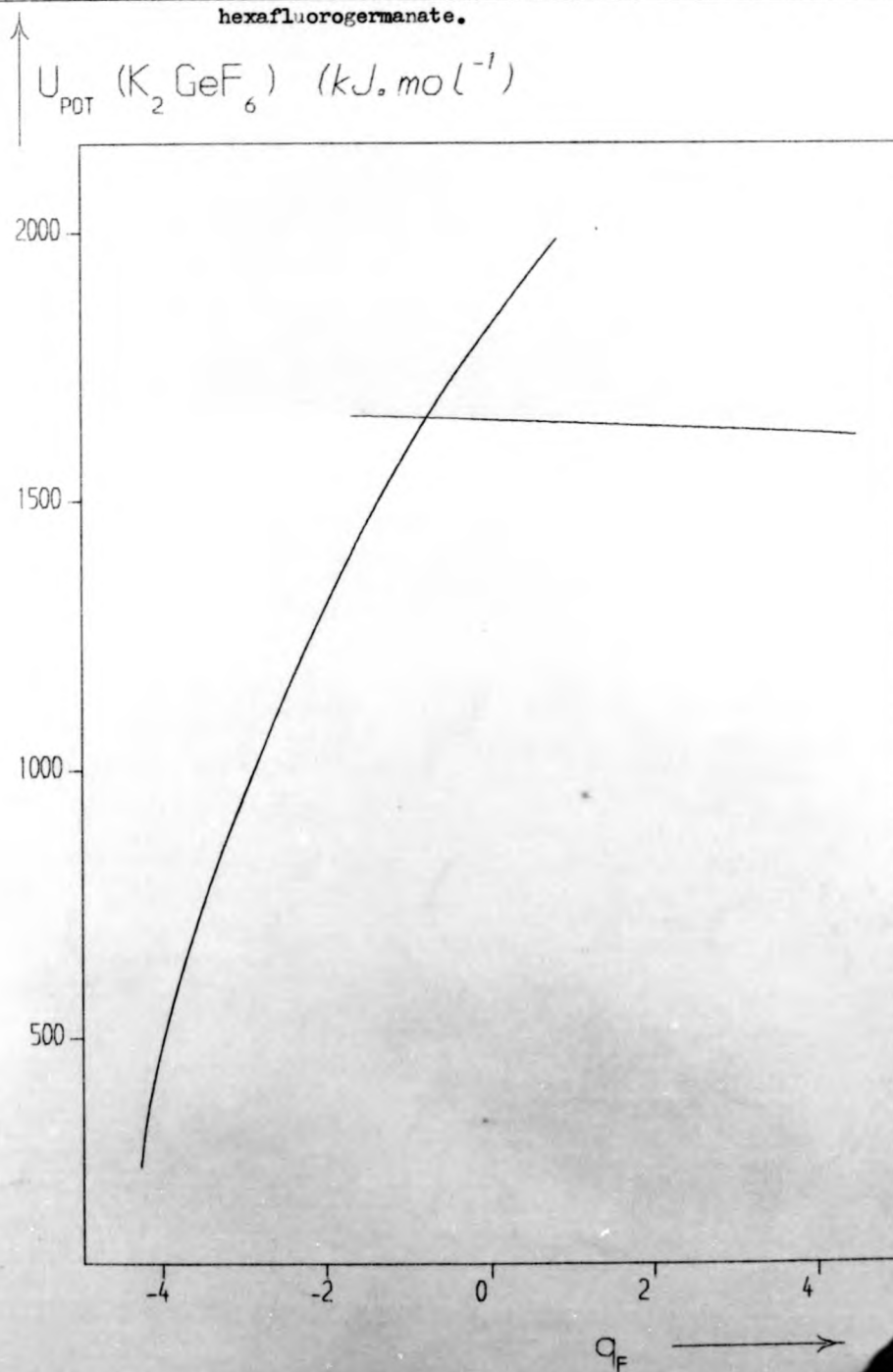
square root is real and the logarithm exists, i.e. not all values of the charge distribution give a solution for the basic radius. As an example the complete curves for the case of potassium hexafluorogermanate are given in Figure 2.8(x). It should be noted that Figure 2.8(i) shows a portion (the portion containing the intersection) of the same curves. There are then two possibilities if the initial choice of parameters are greatly incorrect:

- (a) no intersection point(s) are obtained;
- (b) no solution is obtained for at least one curve within the physically realistic charge range.

The condition (a) could occur if only one curve is obtained or the isotropic assumption is not valid. But (b) is a conclusive situation, and, as can be seen in this section, means the parameters must be extremely badly estimated or the crystal structure is greatly in error.

From these investigations it is seen that the energy minimisation in the new method coupled with flexibility in the potential can be expected to give not only generally reliable results but also some latitude in the assignment of parameters which are, at the current time, difficult to estimate.

Figure 2.8(x) Complete curves for the lattice energy of potassium hexafluorogermanate.



### 3. Computer Programs

#### 3.1 Introduction

The production of results in this research is entirely dependent on the use of computers and extensive computer programming, due to the developed theory, described in Section 2.7, being such as to require computation of lengthy summations. In fact the extensions made by this work in the area of computing are a very large part of the overall progress made.

Some very early parts of this research were performed using the Elliott 4100 series computers at the University of Warwick Computer Centre and the CDC 7600 series computer at the University of Manchester Regional Computer Centre. However by far the majority of the development work and subsequent calculations have been performed using the Burroughs 6700 machine installed at the University of Warwick Computer Centre in 1975. The interactive capabilities of this computer have greatly assisted the rate of program development.

Computer programs

The programming language used mainly throughout this research has been standard Fortran IV, with certain modifications allowed by the Burroughs implementation. Burroughs Algol has also been employed at some stages, although all computer programs described below use the former language.

In this section of the report some of the major programs will be described, with particular emphasis on the complete lattice energy program LATEN. During the course of this research obviously many forms of each program have existed due to the gradual developments made, some indication of the previous forms is given to indicate the direction of the improvements.

Only commonly used and particularly important computer programs are discussed. Countless less important or purely specific programs have been written, often designed to use the interactive facilities available.

### **3.2 LATEN - Lattice Energy Program**

This program has only recently been written as it has resulted from the experience gained in this research by the application of the general method of Section 2.7 to

Computer programs

the various systems discussed in Section 4. The philosophy behind the program is to bring together all stages of the calculation of a lattice energy by this method so that use can be made of the method by chemists not familiar with the complete theory behind it. The major aims are the retention of the flexibility of the method, simplicity of data input and clarity of program output. The unavoidable long computer times necessary for calculation on low symmetry salts give the need for provision inside the program to circumvent problems that this may lead to.

The structure of the program is such that the main body (LATEN) performs the tasks previously performed by hand. It analyses the crystal structure data into the required form, calls the major subroutines for the various stages of the calculation, connects all these sub-sections and controls the course through the program. The major subroutines called are similar in structure to previous programs designed to function autonomously, and their relation to earlier versions is discussed where this is applicable below. The theory used in all sections is as given in Section 2.7. All energies are in kilojoules (from electrons squared per Angstrom) and all distances in Angstroms.

The program takes data from an input file initially and during the course of operation outputs to several files, some of which are used later for input purposes. In Fortran programming code each file is designated by a file number. The files used by the program are given below with their file numbers and a discussion of their use. During the operation of the program in this research it has been standard practice to base these files on magnetic disk, except for the lineprinter output, giving convenience of use.

FILE 1 - This file is subsequently known as the 'electrostatic energy restart file'. The file is opened by the program and need not exist before the program is initiated. It serves two purposes. The first is that during the calculation of the electrostatic terms, periodically (after each increment of the 'h' reciprocal lattice parameter), the variables of the summation are written to the file. This serves the purpose of allowing the summation, if not completed on a first, or subsequent, run, to be restarted from an intermediate point, avoiding unnecessary recalculation. The mechanism for utilising this restart facility is described in the data input discussion. The second function is that at the end of the electrostatic calculations the results obtained are

Computer programs



written to the file for later retrieval by the main body. Each time the file is written to over-writing is performed so keeping the file length to the smallest number of records possible.

FILE 2 - Known as the 'summation restart file'. This performs a similar function to the previous file but for the subroutine SUMS where the repulsion and dispersion summations are performed. The file is updated after completion of the summations for each pair of atom types and the final results output to it after completion.

FILE 5 - The input data file, containing the data as described later.

FILE 6 - The linaprinter output file.

FILE 7 - An 'error' file. Messages are output to this file when certain situations are discovered which may cause failure of the program, incorrect or inaccurate results or a loss of efficiency in calculation. Errors likely to cause failure have the associated message prefixed by the words 'Fatal error'. This file is designed to be listed after completion of the program for diagnostic use. It must be stressed that far from all possible error

situations are foreseen and accompanied by an error message.

FILES 8-11 - The 'results' files. There will be a file made for each repulsion model requested (up to a maximum of four), starting with FILE 8 and so on. Sufficient results are output to each file for the complete solution of the lattice energy calculations using that model. They are primarily used for input data files to plotting or other solution programs (similar to SOLV) after successful completion of LATEN for the salt.

The operation of the main-body, subroutines and functions are discussed below.

Main body, LATEN - This performs all the tasks previously performed by hand when isolated programs were used for the calculations. The crystal structure of the salt is taken as input, as well as the structure of the ions involved. From this the coordinates of the atoms are formulated (using the subroutine DIST) into two parts, one allowed to vary with the unit cell lengths and one which represents a fixed distance (see Section 2.7 - this is necessary for the concept of fixed complex ion geometry). The split is performed by taking the first atom of each ion and finding

Computer programs

the other atoms in the ion by the principle that those atoms nearest are the ones that will constitute the ion. Consequently it is advisable on input of the ion structure (see later) to put the most central atom type first.

The subroutine MULMOM is called which computes and outputs the mono-, di- and quadrupole moments of the unit cell. This is performed as if any of these have a nett non-zero value the electrostatic summations are not necessarily accurate (Redlack and Grindlay (1975)). The necessary action is taken, or advice given, depending on the results.

The requested, and logically required, path is then taken as to the calling of the subroutines DIS, UELEC and SUMS.

The restart files (1 and 2) carrying the results from the subroutines are then input if final results are requested. Also input is the form of each repulsion model required for consideration. For each of these the results file is formed and the subroutine SOLV called; unless no variable radii are present and then a solution for the unknown charge is found.

The program is then terminated.

Subroutine PRGINF - Called by LATEN at the beginning of every run. This gives basic information about the possible options for pathways through LATEN and the levels of print-out possible.

Subroutine DIST - Used by LATEN in the identification of the constituent atoms in complex ions. It computes the distance from one atomic coordinate to a set of others.

Subroutine MULMOM - Called by LATEN, computes the mono-, di- and quadrupole moments of the unit cell, and outputs the feasibility of computing electrostatic energy terms accurately (see above).

Subroutine DTS - Called by LATEN or UELEC, it has three major functions. The first is to output a table of shortest interatomic distances between all the atom coordinates, if this is requested. The second is to find the shortest interatomic distance in the lattice for the purpose of assigning the cut-off radius for the charge density function, and the third is to calculate the overlap energy correction if a Gaussian charge density function is to be used. All these functions are performed

Computer programs

by taking each atom coordinate in turn and finding the shortest distance to all other atoms by searching the adjacent cells.

This subroutine is almost entirely equivalent to one written by Blake (1973) and used in Jenkins and Pratt (1978a).

Subroutine UELEC - Called by LATEN, calculates the electrostatic energy, and cell length derivatives, for a salt. This is basically the program MADELUNG DERIVATIVES described in Jenkins and Pratt (1978a), with some improvements (along with the necessary changes to integrate it into LATEN).

(a) Contains facilities for restarting the summation at intermediate points using the electrostatic energy restart file (file 1, see earlier).

(b) General efficiency of operation improved by the minimisation of the calculations performed inside the cycle.

(c) Now caters for atoms with a charge of zero, which is necessary if atomic positions are not to be considered in this section but are in later subroutines.

(d) The clarity of output has been improved.

The history of development of this subroutine is <sup>that</sup> that the basic structure is of a program written by Blake (1973) to calculate Madelung constants. This program was adapted by Jenkins and Smith, of this department, to calculate results as functions of a charge distribution. The extension to the calculation of cell length derivatives proceeded first for cubic symmetries only and then for rectangular lattices, before the present level of generalisation was obtained.

Subroutine SELF - Called by UELEC, computes the self energies of all the complex ions in the unit cell by Equation 2.2(viii).

Subroutine SUMS - Called by LATEN, computes the repulsion and dispersion summations, and derivative summations, and the dispersion energy terms, with cell length derivatives. The summations are calculated for each pair of types of atom, by taking one atom from each environment of the first type and summing to all the other type of atoms in all cells, until convergence is obtained. Terms internal to complex ions are not considered. After each atom pair has been considered file 2 is updated.

The interatomic distances which are less than a

specified input parameter are output in order to show the coordination number for each atom pair.

This subroutine is a completely re-written version of earlier programs to calculate the simple summations, which were gradually adapted to incorporate derivative summations.

Subroutine SOLV - Called by LATEN, takes as input one of the results files written by the main body. It computes solutions of the equations of the type of Equation 2.7(xvi), for a range of charge previously input, and the intersection points between the curves in this range.

Various forms of this subroutine have been previously written, taking as input slightly different data files. The major of ~~these~~ considered the simple, two different type of repulsion sphere, situation (often sufficient).

Real function S2 - Called by UELEC, returns the value of the square of the maximum reciprocal lattice vector required for a desired degree of convergence. The prediction of this value has been considered by Templeton (1955,1956) and Jenkins (1971,1973) for the uniform and parabolic charge density functions respectively, but only

for a range covering fairly simple lattices. In order to produce a generally applicable Fortran function it was decided to investigate the prediction for all the charge density functions whose use is possible in this program and for a range large enough to include most lattices. This investigation is reported below.

The electrostatic energy of a salt is given by the Bertaut method as:

$$U_{\text{elec}} = \frac{Kq}{RN} \sum_{i=1}^N n_i q_i^2 - \frac{K}{2\pi VN} \sum_h' \frac{|F_h|^2 \phi_h^2}{h^2} + U_{\text{se}} \quad 3.2(i)$$

where all the symbols are defined under Equation 2.7(vi), except the triple indices  $h,k,l$  (indicating reciprocal lattice points) are replaced by the single index  $h$  now indicating a reciprocal lattice vector of length  $h$ . By truncation of the second summation at a reciprocal lattice vector of length  $m$  we introduce an error into the electrostatic energy of:

$$\Delta U_{\text{elec}} = \frac{K}{2\pi VN} \sum_{h>m} \frac{|F_h|^2 \phi_h^2}{h^2} \quad 3.2(ii)$$

(the Gaussian overlap correction also cancels when it is

Computer programs



applicable).

following Templeton (1955) by taking the average value for the structure factor and replacing the summation by an integral this becomes (approximately):

$$\Delta U_{\text{elec}} = \frac{K \sum_{i=1}^N n_i q_i^2}{\pi R N} \int_{\beta}^{\infty} \phi_d^2 da \quad 3.2(\text{iii})$$

where  $d = 2\pi hP$  and  $\beta = 2\pi mF$ . Writing:

$$Q_I = \int_{\beta}^{\infty} \phi_{Ia} da \quad 3.2(\text{iv})$$

where  $I=U$  for uniform,  $I=L$  for linear,  $I=P$  for parabolic and  $I=G$  for Gaussian charge density functions, and using the results for the Fourier transforms of the charge density functions of Templeton (1955), given below, the results for the  $Q$ 's are obtained by repetitive integration by parts.

$$\phi_{Ua} = \frac{3(\sin d - d \cos d)}{d^3} \quad 3.2(\text{v})$$

$$Q_U = \frac{9 \sin^2 \beta}{5\beta^5} - \frac{9 \sin 2\beta}{5\beta^4} + \frac{3(2 + \cos^2 \beta)}{5\beta^3} - \frac{3 \sin 2\beta}{10\beta^2} - \frac{3 \cos 2\beta}{5\beta} - \frac{6}{5} \left( \frac{\pi}{2} - \text{Si}(2\beta) \right) \quad 3.2(\text{vi})$$

Computer programs

where:

$$\text{Si}(x) = \int_0^x \frac{\sin u}{u} du \quad 3.2(\text{vii})$$

This is equivalent to that found by Templeton (1955).

$$\phi_{12} = \frac{12(d \sin \alpha + 2 \cos \alpha - 2)}{d^4} \quad 3.2(\text{viii})$$

$$Q_L = 144 \left[ \frac{4(1 - \cos \beta)^2}{7\beta^7} - \frac{10 \sin \beta (1 - \cos \beta)}{21\beta^6} + \frac{(1 + \cos \beta)(1 - \cos \beta)}{105\beta^5} + \right. \\ \left. \frac{\sin \beta (5 + \cos \beta)}{210\beta^4} + \frac{(\cos 2\beta + 5 \cos \beta)}{630\beta^3} - \frac{(4 \cos \beta + 5) \sin \beta}{1260\beta^2} - \frac{(4 \cos 2\beta + 5 \cos \beta)}{1260\beta} + \right. \\ \left. \frac{1}{252} \left\{ \frac{\pi}{2} - \text{Si}(\beta) \right\} + \frac{2}{315} \left\{ \frac{\pi}{2} - \text{Si}(2\beta) \right\} \right] \quad 3.2(\text{ix})$$

$$\phi_{p2} = \frac{60(d \cos \alpha - 3 \sin \alpha + 2\alpha)}{d^5} \quad 3.2(\text{x})$$

$$Q_p = 3600 \left[ \frac{\sin^2 \beta}{\beta^9} - \frac{\sin \beta (3 + \cos \beta)}{2\beta^8} + \frac{(9 + 5 \cos \beta)}{14\beta^7} - \frac{5 \sin \beta}{84\beta^6} - \frac{\cos \beta}{84\beta^5} + \right.$$

$$\left. \frac{\sin \beta}{336\beta^4} + \frac{\cos \beta}{1008\beta^3} - \frac{\sin \beta}{2016\beta^2} - \frac{\cos \beta}{2016\beta} + \frac{1}{2016} \left\{ \frac{\pi}{2} - \text{Si}(\beta) \right\} \right] \quad 3.2(\text{xi})$$

Agreeing with the result of Jenkins (1971) and:

$$\phi_{G2} = \left[ \exp\left(\frac{\beta^2}{4\pi^2}\right) \right]^{1/2} \quad 3.2(\text{xii})$$

$$Q_G = \pi^{3/2} \text{erfc}\left(\frac{\beta}{2\pi}\right) \quad 3.2(\text{xiii})$$

where:

$$\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du \quad 3.2(\text{xiv})$$

Computer programs

For  $n$  decimal places of accuracy in the electrostatic energy:

$$\Delta U_{\text{ELEC}} \leq 0.5 \times 10^{-n} \quad 3.2(\text{xv})$$

So the maximum value of  $P$  (and hence the reciprocal lattice vector) required is given by:

$$0.5 \times 10^{-n} = \frac{K P}{\pi R} Q_I \quad 3.2(\text{xvi})$$

where  $P$  is the lattice parameter,

$$P = \frac{\sum_{i=1}^M n_i q_i^2}{N} \quad 3.2(\text{xvii})$$

and  $R$  is the cut-off radius of the charge density function.

These equations are not solved but curves of  $\beta$  against  $P$  drawn for the various  $I$  and different values of  $n$ . The curves for  $n=-2$  to  $2$  and  $I=0$  are given in Figure 3.2(i). The other charge density functions are considered for  $n=-2$  to  $3$  and for  $I=L$  are plotted in Figure 3.2(ii),  $I=P$  in Figure 3.2(iii) and  $I=G$  in Figure 3.2(iv). The maximum  $P/R$  value considered in each case is 100, and is

Computer programs

Figure 3.2(i) Convergence of electrostatic energy using a uniform charge density function.

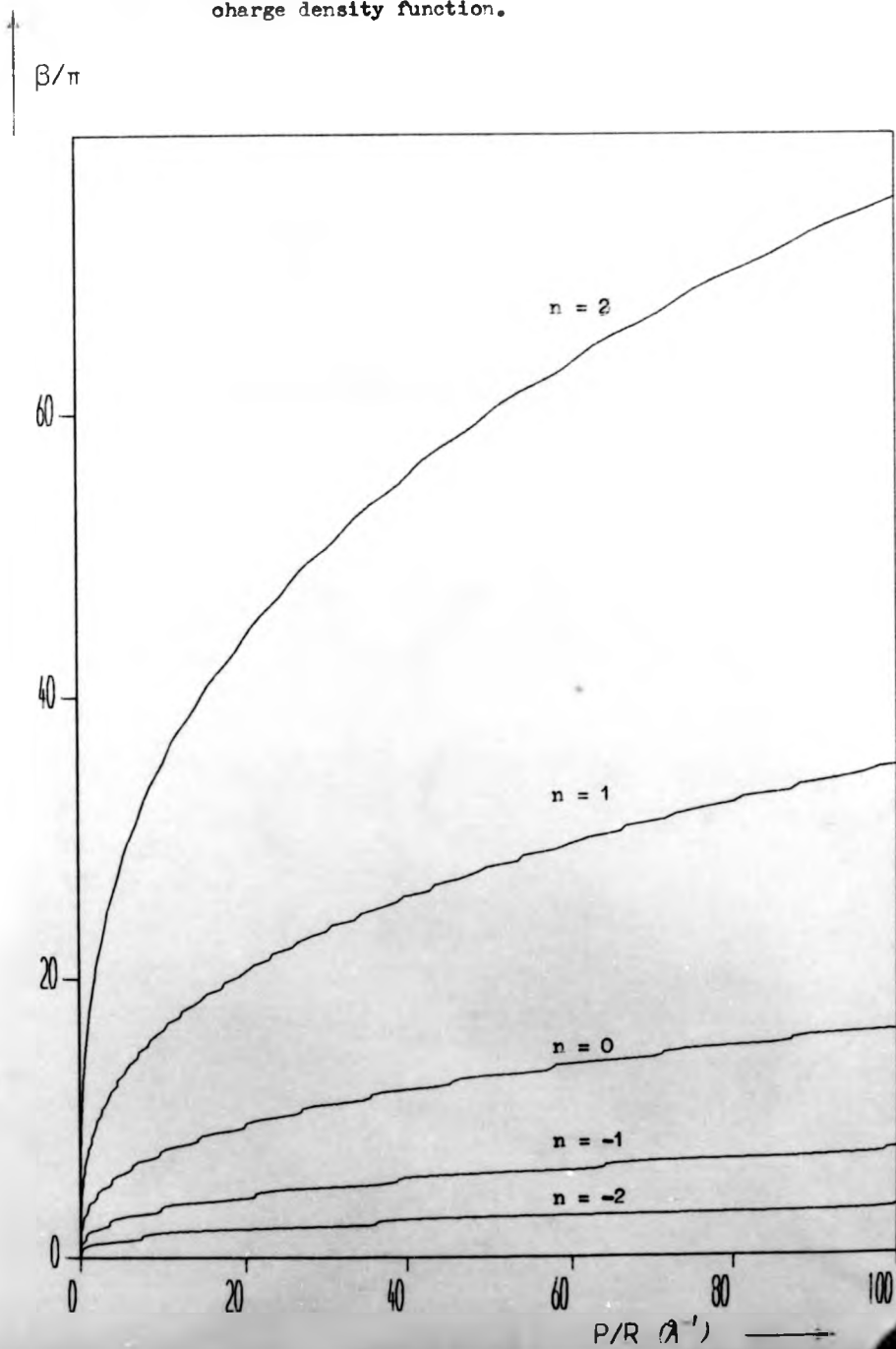


Figure 3.2(ii) Convergence of electrostatic energy using a linear charge density function.

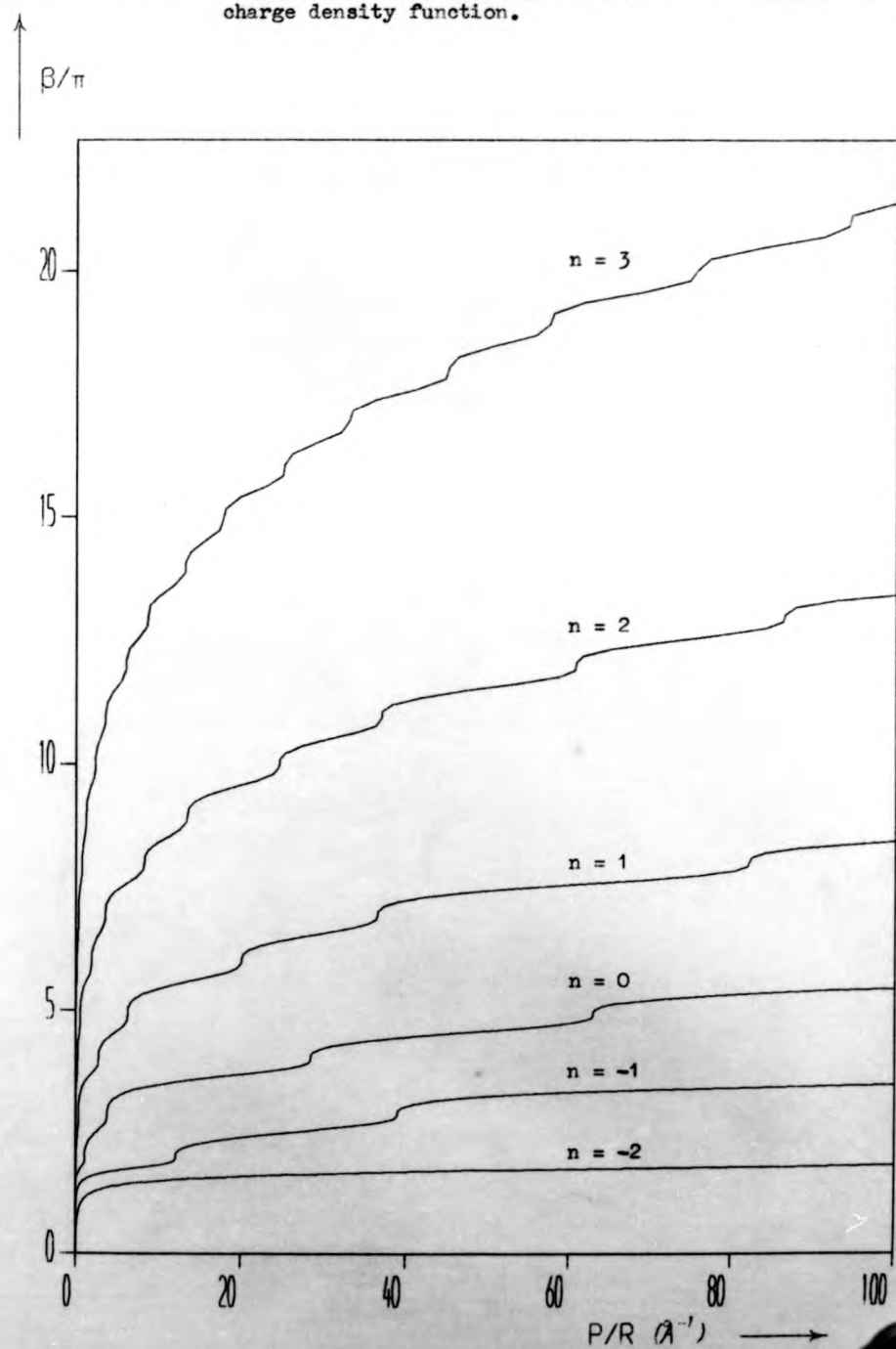


Figure 3.2(iii) Convergence of electrostatic energy using a parabolic charge density function.

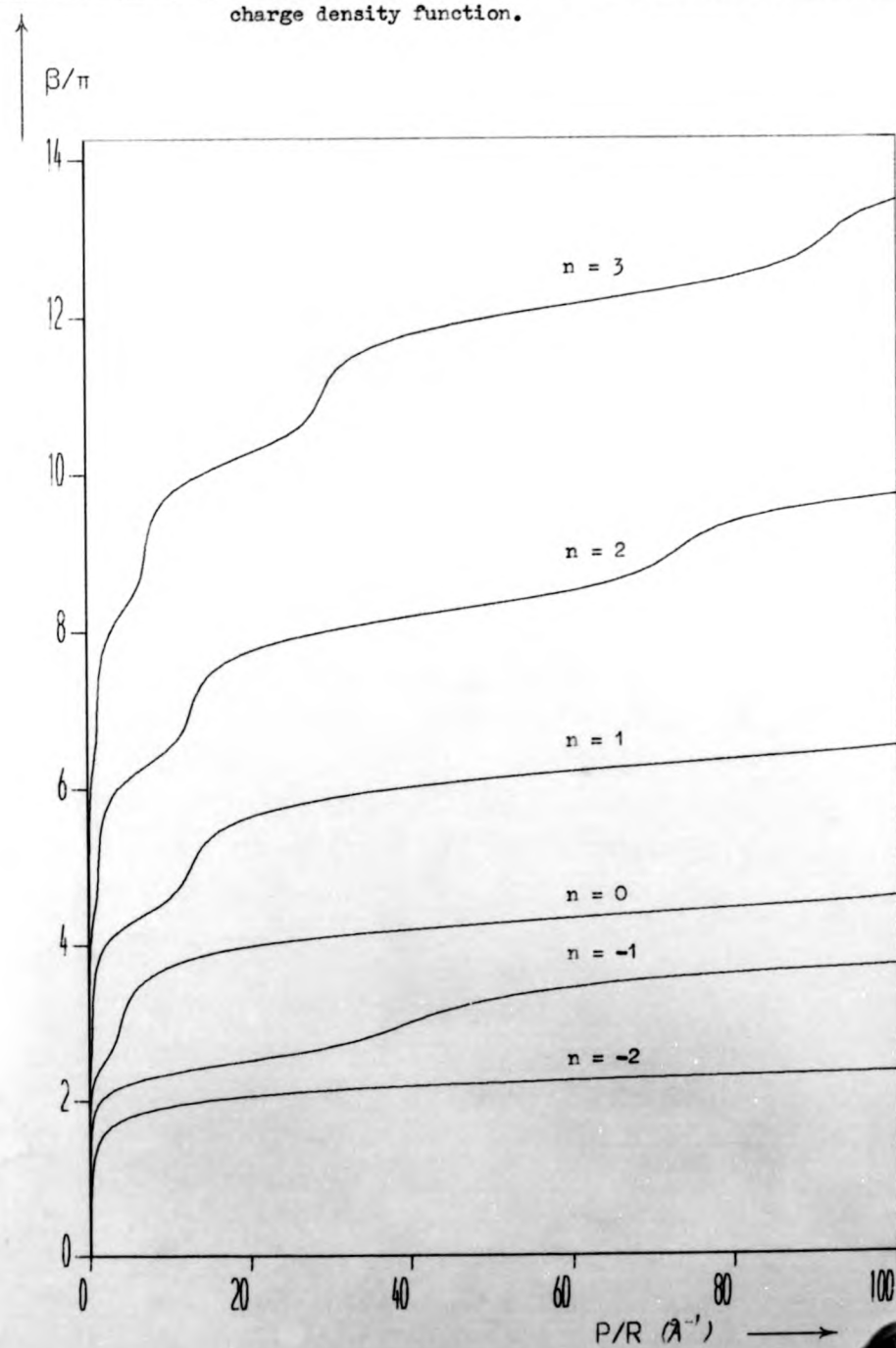
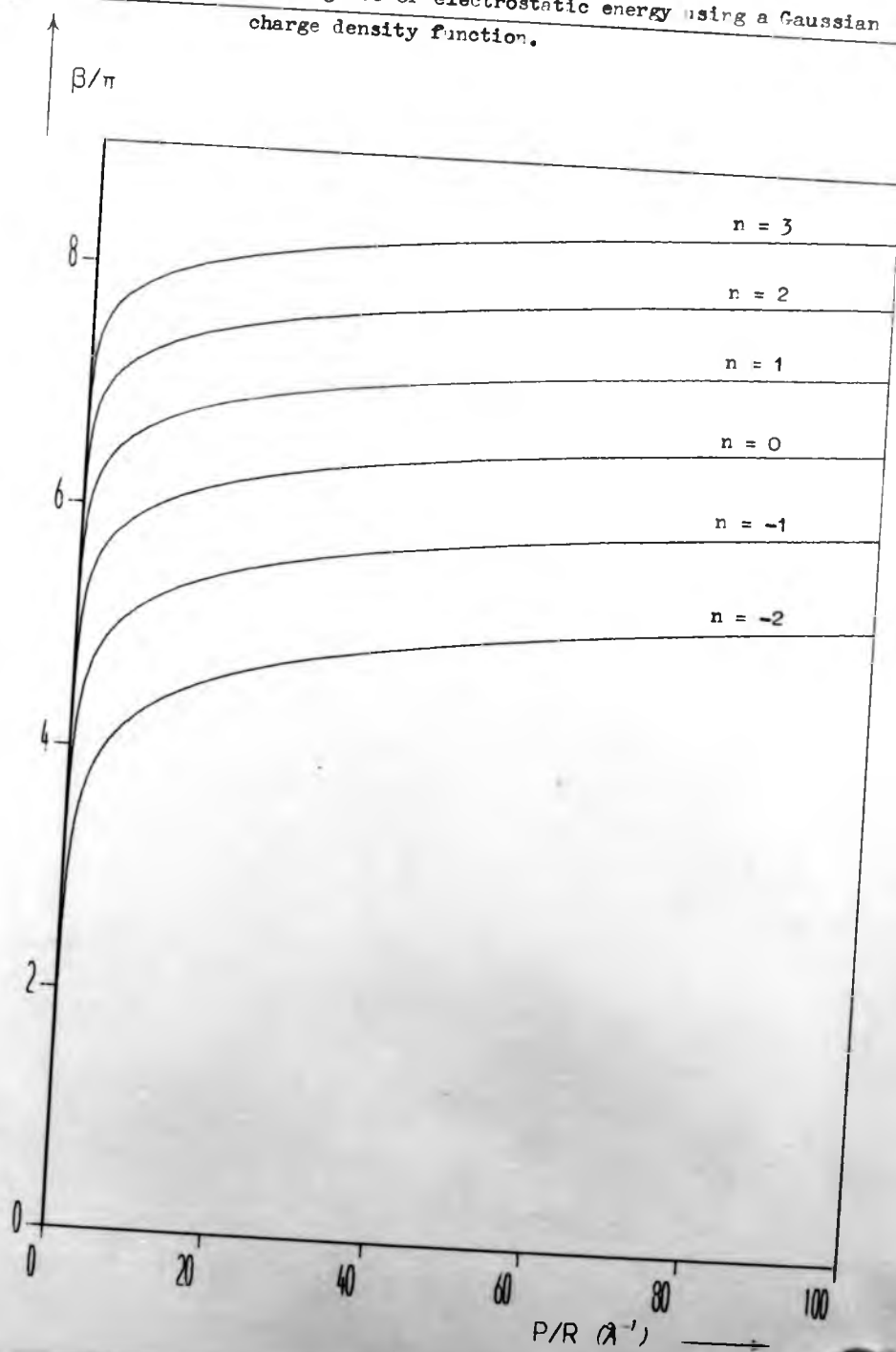


Figure 3.2(iv) Convergence of electrostatic energy using a Gaussian charge density function.



an extension to the work of Jenkins which considered a maximum of only 10. Virtually all lattices should be included by this range.

The above figures show that generally for convergence to high accuracy the Gaussian function is the most efficient, closely followed by the parabolic. For rough estimates though this is not necessarily true. The fact that cell length derivatives are not calculated by the program if a Gaussian function is used (due to the overlap correction) means that the parabolic should be adopted generally, as is done throughout this work.

For the purposes of the Fortran function, rough linear relationships are taken from the above figures, ensuring that these lines always lie above the curves they approximate, and the maximum reciprocal lattice vector required is estimated from the knowledge of the lattice parameter, the cut-off radius and the desired convergence.

Real function SHAPE - Called by UELEC. As written by Blake (1973), returns the value of  $g$  (Equation 2.7(vi)) dependent on the charge density function.

Real function PHISQD - Called by UELEC, returning the

Computer programs



square of the Fourier transform of the charge density function. As written by Blake (1973).

Real function DPHSQD - Called by OELEO, returning the derivative of the square of the Fourier transform of the charge density function with respect to the square of the reciprocal lattice vector. As used in MODELING DERIVATIVES.

A description of the data necessary for a full run of the program follows, described record by record. The Fortran IV data format required by the program is given in brackets.

The first record (2I2) consists of two integer parameters, the first (IR) controls the route through LATEN and the second the level of print-out produced. If IR is negative the program is to be restarted from an intermediate point in the calculations. Details of the function of these parameters are given by the subroutine PRGINF.

The second record (12A6) contains the running title, usually the compounds name. The third (3F9.6) the unit cell lengths, the fourth (3F9.6) the unit cell angles or

cosines and the fifth (I2) the number of molecules per unit cell.

The sixth record (A1,I3,I2) contains the space group information. The first item is a letter (P,A,E,C,I,F or F) indicating the symmetry of the lattice. If other than P the equivalent positions implied will be automatically generated (see later). The next item is the space group number and the third is 0 for a centrosymmetric cell and 1 if non-centrosymmetric. This symmetry information allows the omission of unnecessary terms of the summation (absent or cancelled).

The seventh record (I2) contains the number of Hyckoff position sets to be used. (If this number is zero or less the coordinates should be input explicitly.) Following this the sets are given, the first record (I2,A1) giving the number of equivalent positions and a designated letter. The number of positions, on separate records (3(F6.4,4A1)), to be input is the number on the first record modified by the symmetry information. Positions linked by either the symmetry (in non-primitive cells) or centrosymmetry (when stated above) to a previously quoted position should not be input as well, they are produced automatically. Each coordinate of each

position given has the form of a constant followed by four symbols, the first and third may be either +, - or space, the second and fourth x, y, z or space. The meaning being obvious when familiar with the Wyckoff notation outlined in the 'International Tables for X-ray Crystallography'.

Following the input of all equivalent positions comes a record (I2) giving the number of different types of ion (complex counted as one). Then this number of records (I2,1X,5(A2,I2)) giving the structure of these ions. The first number of these records being the number of different types of atom in the ion, followed by each of their symbols and the number in each ion (e.g. for the hexachloroplatinate(IV) ion - 2 PT 1CL 6).

Immediately after this comes a group of records for each of the chemical symbols used above, in the same order. The first containing (A2,F7.3,I2) the symbol, the charge it carries (if inside a complex ion the largest distribution of charge should be used) and the number of sets of equivalent positions which have these atoms in their positions. A pair of records follow for each of these sets; the first of each pair (I2,A1) stating the Wyckoff symbol and the second (3F6.4) the values of the variables x, y and z used in the definition of the

equivalent positions.

This is the end of the crystal structure data and following comes the particular electrostatic energy parameters. The first record of which (4I2,F6.2), when the first number is zero, implies a parabolic charge density function is used with maximum convergence and the maximum reciprocal lattice vector is computed by the function S2. If non-zero the other parameters represent the number of decimal places of convergence (-2 to 3), the charge density function (0-uniform, 1-linear, 2-parabolic, 3-Gaussian), if an overlap energy correction is required (1 if yes, 0 if not, only for Gaussian) and the square of the maximum reciprocal lattice vector (if less than or equal to zero it will still be estimated by S2). The second record (F9.6) contains twice the cut-off radius of the charge density function, if input as zero it is computed by subroutine DIS. The third (I2,2(2Y,A2),F7.3) gives first the number of variable charges as 0, 1 or 2. If 0 the remainder of the record is ignored, if 1 the symbol of this variable charge is given next, if 2 the two symbols followed by a value for the second charge to be used in order to calculate the final results. The number of types of atom records follow (3F6.3) containing the charge on this atom as a function of the variables, the

Computer programs

first number a constant, the second the coefficient of the first variable and the third the coefficient of the second variable.

The summation and dispersion parameters follow this. First (F6.4) the repulsion exponent (in Angstroms) and second (F4.1) the upper limit of the distances required to be output. The number of types of atom records (3F7.3) follow containing the dispersion coefficients; the polarisability, characteristic energy and electron number (in the units quoted in Section 4.2), all zero if the ion is not to be considered.

The data pertaining to the repulsion models follow. Firstly (3F7.3) the charge range (minimum, maximum, increment) and secondly the number of models (I2). For each model a group of records follows. The first (9A6) gives a title for the model and then the number of types of atom records (I2, F6.3, 2F7.3, F4.1) follow. If the first number is zero the rest of the record is ignored and the atom type is not considered in the repulsion model. If 1 then it is considered as a constant with the basic radius, charge (constant and coefficient of the variable) and electron number given after. If 2 it is considered as a variable basic radius with the parameters (radius input

irrelevant) following.

This is the end of the input, a sample deck of data is given in Table 3.2(i) where the asterisks merely indicate the left-hand side for clarity. The data is for potassium hexachloroplatinate, the crystal structure is taken from Wyckoff (1965). The test data in the table produces the results given in Section 4.6 for this salt. Considering the complexity of the calculations the relative simplicity of the input data is one of the strong points of the program and makes its use by all chemists possible.

The level of lineprinter output can be chosen by the user, from nil to very high. Generally it is best to choose a level giving just sufficient information throughout the calculations to follow its progress, and not just at the final results stage.

### **3.3 Graph Plotting**

The University of Warwick Computer Unit has implemented a limited form of the plotting package 'Ghost' produced by workers at Culham, called 'Minighost', on the Burroughs 6700 computer. The routines this contains have

Computer programs

Table 3.2(i) Sample data input for LATE4, to use the full facilities of the program.

\* 1 3  
\*POTASSIUM HEXACHLOROPLATINATE(IV)

\* 9.755 9.755 9.755

\* 0.0 0.0 0.0

\* 4

\*F225 (

\* 3

\* 4A

\*0.0 0.0 0.0

\* 8B

\*0.25 0.25 0.25

\*240

\*0.0 +X 0.0 0.0

\*0.0 0.0 +X 0.0

\*0.0 0.0 0.0 +X

\* 2

\* 1 K 1

\* 2 PT 1CL 6

\*K 1.000 1

\* 8B

\*0.0 0.0 0.0

\*PT 4.000 1

\* 4A

continued over

Results

Table 3.2(i) continued

\*0.0 0.0 0.0

\*CL -1.000 1

\*240

\*0.24 0.0 0.0

\* 0

\* 0.0

\* 1 CL

\* 1.000 0.000

\*-2.000 -6.000

\* 0.000 1.000

\*0.345

\* 5.0

\* 1.029 45.84 8.0

\* 0.0 0.0 0.0

\* 2.995 17.2 8.0

\* -1.0 0.0 0.05

\* 2

\*SPHERICAL ANION MODEL

\* 1 1.191 1.0 0.0 8.0

\* 2 0.0 -2.0 0.0 8.0

\* 0

\*SIX SPHERE MODEL

\* 1 1.191 1.0 0.0 8.0

\* 0

\* 2 0.0 0.0 1.0 8.0

Results



been used to write plotting programs as supplements to the program LATEX, and for many other uses. The products of which are reproduced in this report. Graph plotting routines have not been included implicitly in LATEX due to machine dependence of graphics procedures and the widely differing requirements from salt to salt for the type of visual representation required.

The major plotting program written during this research, and the only one described here, takes as input results files identical, or similar, to those produced by LATEX and outputs graphs of basic radius, lattice energy and/or a thermodynamic parameter against charge distribution, along with diagnostic information concerning the graphs.

The method used is of solution of the equations for each curve and the storing of the points (approx. 200 for each curve) in arrays. The program plots the required curves by cubic spline fitting between points onto axes annotated and labelled by subroutines written as part of this research. The curves are not individually labelled but lineprinter output is produced giving the order at the ordinates, so enabling identification. Other diagnostic subroutines compute all the intersection point coordinates

Computer programs

and the point of closest approach of all the curves.

Input to the program, aside from the results files, is minimal. A few simple parameters describing which plots are required, the charge range for the abscissa and linear relationships between lattice energy and thermodynamic parameter, if this is required. Aside from these parameters characters to be output as labels to the axes are the only other input.

The program is generally flexible enough to produce graphs for most lattice energy studies. Although another form is needed when no variable charge is involved (see Section 4.9) and lattice energy (or other) curves are plotted against the variable ion basic radius.

### **3.4 Bond Lengths and Bond Angles**

A reasonably simple program for the calculation of interatomic distances and angles between interatomic vectors has been written, primarily designed for interactive use. This is used to test and investigate crystal structure data prior to input into LATEN.

The input is simply a title, the unit cell

dimensions, a set of atomic coordinates and a list of bond angles required. All (shortest) interatomic distances are output and the necessary interatomic vectors retained in order to calculate the bond angles, output after.

### **3.5 Atomic Coordinate Computation**

In some cases, generally the fixing of atoms not found in the crystal structure studies (often hydrogen), it is desirable to compute an atomic position that would satisfy, as closely as possible, certain geometrical constraints, in terms of bond lengths and bond angles. A general program has been developed for this purpose, taking as input the unit cell parameters and geometrical constraints. The program is again designed so that it can be used interactively if desired.

### **3.6 Multipole Moment Expansion**

A computer program used to calculate coefficients for the multipole moment expansion of Madelung constants, using the Ewald method, was obtained from Austria at the beginning of this research, where it was written by Herzig, Kuzmany and Neckel (1970). Before the differentiation of the Bertaut method, expansions of this

Computer programs

type were the only source available for obtaining the cell length derivatives of the electrostatic energy term, and so much use of the program was made at that time. The extensive manipulation required to prepare data for input and the substantial calculations required to produce coefficients from the output data made the program inefficient and tiresome to use. Work was carried out during this research to write extensions to the basic program in order to remove these larger inconveniences. A certain amount of success was obtained for the application of the program to azide and difluoride salts, however the extensions failed to prove generally applicable. The complexity of this method led to these efforts being abandoned in favour of the differentiation of the Bertaut method, and was in fact a major factor in motivating the exploration of this possibility.

Computer programs

## **4. Results**

### **4.1 Introduction**

The results of calculations performed during this research are reported here in approximate chronological order. Results which have been previously reported are not repeated, however they are usually extended to include calculations using the newly proposed method (Section 2.7) and, if available, more recent experimental data. Early calculations were performed using the potential chosen in Section 2, without any energy minimisation conditions being imposed, after these came calculations using the Jenkins and Waddington equation (Section 2.5). Immediately following this work calculations using the energy minimisation conditions applied to the chosen potential were started. The majority of these calculations were performed before the unification of the necessary computational stages into the program LATEN.

The calculations are performed, and reported, for each ion taking a specific sequence of steps, described consecutively below for a general situation.

#### **Results**

(a) The available crystal structures of salts involving the ion under study are abstracted from the literature - if the structure is completely resolved and accurate, if the ion retains a 'near gaseous' configuration and if the compound can be considered as ionic for the purposes of the calculations.

(b) A distribution of charge in the ion, between the constituent atoms, is assumed and the electrostatic component of the lattice energy, and its different cell length derivatives, are calculated as quadratic functions of one of the charges of this distribution (all complex ions considered in this work contain only two different atom types). These calculations are performed using the computer program MADELUNG DERIVATIVES (Jenkins and Pratt (1974a)), or others similar to this.

(c) The dispersion energy terms and cell length derivatives are next computed. A dispersion model is chosen as the most likely to approximate the true situation, for which the necessary data for the calculation is available. A polarisability set is chosen and the other dispersion parameters estimated as well as is possible. The necessary summations are readily obtained from the crystal structure.

(d) A repulsion model (or models) for the ions is chosen as that composed of spheres of known basic radii and one

## Results

type of sphere of unknown basic radius which best approximate the true repulsion envelopes of the ions. The necessary summations are readily performed from the crystal structure.

(e) Each different derivative with respect to a cell length, on calculation, gives an equation involving the unknown basic radius and the unknown charge on one type of atom in the complex ion. Each value of the charge distribution then implies up to three values for the unknown basic radius, which in turn each imply a value for the lattice energy.

(f) Use of the equations from (e) allows a plot of the lattice energy of each salt against the unknown charge on one type of atom in the complex ion. The intersection points of these figures give both values for the lattice energy, this charge and the basic radius. (N.B. This necessarily assumes an isotropic situation for the unknown basic radius).

(g) A thermochemical cycle can also be resorted to which relates the individual lattice energies to a thermochemical property of the complex ion (most commonly half of the cycle in Figure 1.3(i), the thermochemical property being the enthalpy of formation of the gaseous ion). This allows the combination of all the curves of (f) onto common axes. From this we can assign a value for the

#### Results

thermochemical property. This process can be repeated for more than one thermochemical cycle.

This is the approach taken in the following sections.

The numerical results are not reported completely. The parameters used and summations performed which are not reported are considered not to warrant the large amount of space that they would occupy. The bulk of this data would tend to smother the major points of the studies whilst giving little, if any, supplementary information. In the studies reported all the major terms are quoted, they are sufficient to formulate the individual contributions to the lattice energy, and its cell length derivatives, completely.

The studies on individual complex ions are preceded by a study describing the evaluation of basic radii for common ions. These values are used in step (d) above.

#### **4.2 Evaluation of Basic Radii**

The newly proposed method (Section 2.7) was developed to calculate lattice energies, thermodynamic parameters and complex ion charge distributions. However during the

#### **Results**



process of calculation it is necessary both to know a basic radius (or radii) and to calculate one. It seems logical then that some initial calculations should be designed to predict basic radii for some simple ions and that these calculations should be based on the method itself.

This approach was adopted at the outset, considering the alkali halide salts to predict basic radii for alkali metal and halide ions (Jenkins and Pratt (1977a)), as had been done by Higgins and Mayer (1933) nearly fifty years ago. For these simple cubic salts, involving only monatomic ions the equation below is produced by the energy minimisation condition (using the potential selected in Section 2).

$$\rho(U_{elec} + 6U_{dd} + 8U_{qd}) = \frac{1}{2}bc_{++}\exp\left(\frac{2\bar{r}_+}{\rho}\right)\sum_i^{ions} R_{ii}\exp\left(-\frac{R_{ii}}{\rho}\right) + \\ bc_{+-}\exp\left(\frac{\bar{r}_+ + \bar{r}_-}{\rho}\right)\sum_i^{ions} R_{ii}\exp\left(-\frac{R_{ii}}{\rho}\right) + \frac{1}{2}bc_{--}\exp\left(\frac{2\bar{r}_-}{\rho}\right)\sum_i^{ions} R_{ii}\exp\left(-\frac{R_{ii}}{\rho}\right) \quad 4.2(1)$$

which can be expressed as:

$$ax^2 + bxy + cy^2 = d \quad 4.2(ii)$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are calculable constants

## Results

independent of basic radii:

$$x = \exp(\bar{r}_+/ \rho) \quad 4.2(11i)$$

and

$$y = \exp(\bar{r}_- / \rho) \quad 4.2(iv)$$

we have twenty such equations, involving nine unknowns (at a single rho value), when considering the twenty alkali halides. These could be solved by an iterative method (see later) but by choosing one radius a set of solutions can be obtained which give as good a solution as any other. Many such sets of solutions were calculated and published in Jenkins and Pratt (1976b). Groups of equations were solved for five different sets of polarisability data (Pauling (1927); Tesson, Kahn and Shockley (1953); Pirenne and Kartheuser (1964); Michael (1969); Jaswal and Sharma (1973)), different sets of electron numbers and different values of the repulsion exponent (0.33, 0.345, 0.36 & 0.38). Solutions were obtained by choice of the basic radius of sodium as compatible with the work of Huggins and Mayer (1933). The full results are presented in the above reference. The logic for the existence of these multitudinous sets must be brought into

## Results

question in view of the results of Section 2.8 regarding the dependence of lattice energy (calculated using the new method) on the initial choice of basic radius. This low lattice energy dependence after minimisation explains the lack of unique solutions to the groups of equations which was found above.

Only the sets corresponding to the polarisability data of Pauling (1927), Tessman et al (1953) and Pirenne and Kartheuser (1964), the electron numbers as the number of valence electrons and the repulsion exponent as 0.345 Å are used further in this work. As the polarisabilities of Pirenne and Kartheuser are preferred to all others this is the most commonly used set.

Although basic radii for alkali metal (and halide) ions are the most commonly used, ideally values should exist for all common monatomic ions. It was decided to extend the above calculations to include both alkaline earth metal and chalcogenide ions. Having questioned the necessity of many different sets of radii it was decided to continue calculations to produce only one set, considering all the ions previously mentioned. Only salts crystallising as simple cubic structures are considered, non-cubic salts have a tendency to show greater covalency

## Results

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## Results

and anisotropy (non-spherical ions). The Madelung constants of all these structures are well known (Laddington (1959)). Polarisability data from Pauling is taken as Pirenne and Kartheuser do not quote values for the additional ions. The coefficients used to calculate dispersion energies are listed in Table 4.2(i), the electron numbers used are simply the number of valence electrons. From this data and the crystal structures (taken from Wyckoff (1965), except for rubidium selenide which is from Sommer and Hoppe (1977)) we can produce, for each salt, an equation of the form of Equation 4.2(ii). There are 58 simple cubic salts (out of a possible 60) and hence 58 equations:

$$a_i x_j^2 + b_i x_j x_k + c_i x_k^2 = d_i \quad 4.2(v)$$

where  $i$  runs from 1 to 58,  $j$  signifies one of the ten cations and  $k$  one of the eight anions, are obtained. No two equations have identical indices  $j$  and  $k$  (i.e. no salt has two simple cubic pleomorphs). The coefficients of these equations are listed in Table 4.2(ii). In order to find the best set of solutions for the group of equations a least squares approach is adopted. Reformulating each equation by associating with each an error ( $e_i$ ):

$$a_i x_j^2 + b_i x_j x_k + c_i x_k^2 - d_i = e_i \quad 4.2(vi)$$

## Results

Table 4.2(i) Coefficients for the calculation of the dispersion energy for salts composed of some simple monatomic ions.

Ion	$\alpha(P)^* (\text{\AA}^3)$	$\alpha(PK)^* (\text{\AA}^3)$	$\epsilon^+$
Li <sup>+</sup>	0.029	0.029	109.0a
Na <sup>+</sup>	0.179	0.291	82.6a
K <sup>+</sup>	0.83	1.029	45.8a
Rb <sup>+</sup>	1.40	1.570	39.6a
Cs <sup>+</sup>	2.42	2.641	36.2a
Be <sup>2+</sup>	0.008	-	221.8b
Mg <sup>2+</sup>	0.094	-	115.5b
Ca <sup>2+</sup>	0.47	-	73.8b
Sr <sup>2+</sup>	0.86	-	62.4b
Ba <sup>2+</sup>	1.55	-	51.2b
F <sup>-</sup>	1.04	0.881	24.7c
Cl <sup>-</sup>	3.66	2.995	17.2c
Br <sup>-</sup>	4.77	4.138	15.0c
I <sup>-</sup>	7.10	6.240	12.8c
O <sup>2-</sup>	3.88	-	12.5d
S <sup>2-</sup>	10.2	-	6.2d
Se <sup>2-</sup>	10.5	-	8.2d
Te <sup>2-</sup>	14.0	-	6.9d

continued over

Results

Table 4.2(i) continued

Ion	$\Delta(F)^* (\text{\AA}^3)$	$\Delta(PK)^* (\text{\AA}^3)$	E <sup>a</sup>
NH <sub>4</sub> <sup>+</sup>	-	1.656	41.1e
Tl <sup>+</sup>	-	1.880	29.4a

\* F - Pauling (1927); PK - Pirenne and Kartheuser (1964)

+  $\times 10^{-12}$  erg.molecule<sup>-1</sup>

a 90% of second ionisation potential

b 90% of third ionisation potential

c obtained from the experimental data of Mayer (1933)

d estimated from Pritchard's (1953) values for the second electron affinity of X

e Goodliffe et al (1971)

## Results

Table 4.2(ii) Coefficients of Equation 4.2(vi) for cubic salts ( $\text{kJ.mol}^{-1}.\text{\AA}^{-1}$ ).

Salt	*	$a_i$	$b_i$	$c_i$	$d_i$
LiF	1	0.3986855690	2.1875752430	0.1495070884	329.947
LiCl	1	0.0406920496	0.4302095590	0.0152595186	223.515
LiBr	1	0.0189336496	0.2500887311	0.0071001166	197.310
LiI	1	0.0067940634	0.1210291111	0.0025477738	172.643
NaF	1	0.0727575036	0.6603086242	0.0436545022	254.345
NaCl	1	0.0088871135	0.1484892663	0.0053322681	181.845
NaBr	1	0.0044862154	0.0915132078	0.0026917292	164.263
NaI	1	0.0016085778	0.0442889023	0.0009651467	143.564
KF	1	0.0162542109	0.2277672306	0.0097525265	202.718
KCl	1	0.0023268916	0.0575061079	0.0013961349	153.897
KBr	1	0.0012390070	0.0368192757	0.0007434042	140.846
KI	1	0.0004767268	0.0167361853	0.0002860361	124.716
RbF	1	0.0086973493	0.1486103939	0.0053384096	190.946
RbCl	1	0.0012882683	0.0378489313	0.0007729610	146.696
RbBr	1	0.0007357649	0.0254670684	0.0004414589	136.525
RbI	1	0.0002704100	0.0125468273	0.0001622460	119.538
CsF	1	0.0041822206	0.0870033837	0.0025093324	181.259
CsCl	2	0.0043132990	0.0387401434	0.0025879764	249.265
CsBr	2	0.0026795040	0.0257277872	0.0016077024	232.314
CsI	2	0.0011820405	0.0127153239	0.0007092243	205.545
$\text{Li}_2\text{O}$	3	3.1117345800	2.9550170700	0.0145816049	857.270
$\text{Li}_2\text{S}$	3	0.2939643896	0.5900421695	0.0030946946	560.693

continued over

Results



Table 4.2(ii) continued

Salt	*	$a_1$	$b_1$	$c_1$	$d_1$
LiSe	3	0.1882166262	0.4054563395	0.0016811622	512.843
LiTe	3	0.0894791174	0.2161852009	0.0006035224	453.296
NaO	3	0.2914900480	0.4414044615	0.0021411695	586.040
NaS	3	0.0541280601	0.1471960246	0.0005768755	419.354
NaSe	3	0.0355957838	0.1030971045	0.0003227704	389.821
NaTe	3	0.0169063273	0.0546426567	0.0001145571	345.868
N <sub>2</sub>	3	0.0773333773	0.1442498058	0.0003469558	466.179
N <sub>2</sub> S	3	0.0150967388	0.0496034858	0.0000978229	340.636
N <sub>2</sub> Se	3	0.0099352203	0.0346751121	0.0000545285	319.689
N <sub>2</sub> Te	3	0.0049486444	0.0190721431	0.0000205478	289.062
RbO	3	0.0492751768	0.0983895997	0.0001859283	450.512
RbS	3	0.0103213870	0.0358262573	0.0000575145	333.051
RbSe	3	0.0060113800	0.0225388448	0.0000269892	303.924
CaF <sub>2</sub>	3	0.0153656310	0.7242398890	0.1596189516	624.852
SrF <sub>2</sub>	3	0.0076910586	0.4729693462	0.0960448809	564.362
SrCl <sub>2</sub>	3	0.0006864411	0.1073500511	0.0166718159	425.902
BaF <sub>2</sub>	3	0.0033785843	0.2853146973	0.0527356379	505.290
BaCl <sub>2</sub>	3	0.0003258258	0.0679966252	0.0097632812	390.298
BeS	4	0.1086036630	1.2297565500	0.0181006105	875.736
BeSe	4	0.0690030174	0.9263182529	0.0115005029	828.820
BeTe	4	0.0262278441	0.5108930349	0.0043713074	740.264
MgO	1	0.2035845635	1.2079982690	0.0678615212	1289.510

continued over

Results

Table 4.2(ii) continued

Salt	*	$a_1$	$b_1$	$c_1$	$d_1$
M <sub>2</sub> S	1	0.0262182315	0.2809178326	0.0087394105	843.219
M <sub>2</sub> Se	1	0.0158454723	0.1965751308	0.0052818241	785.157
CaO	1	0.0589127934	0.4951341485	0.0196375978	990.593
CaS	1	0.0096280545	0.1381164870	0.0032093515	697.928
CaSe	1	0.0061302528	0.1003277078	0.0020434176	661.452
CaTe	1	0.0025092567	0.0533180989	0.0008364189	596.725
SrO	1	0.0286514885	0.2951719412	0.0095504962	871.783
SrS	1	0.0048924358	0.0855236385	0.0016306286	624.822
SrSe	1	0.0031774170	0.0630118292	0.0010591350	596.535
SrTe	1	0.0019414191	0.0444673190	0.0006471357	590.006
BaO	1	0.0135804692	0.1762216460	0.0045268231	782.059
BaS	1	0.0022996314	0.0501266582	0.0007665438	562.278
BaSe	1	0.0014868084	0.0368192757	0.0004956028	538.099
BaTe	1	0.0006734697	0.0210281848	0.0002244859	497.305

\* structure type, see below

- 1 sodium chloride structure
- 2 cesium chloride structure
- 3 calcium fluoride structure
- 4 zinc sulfide structure

Results

we can minimise the function (F):

$$F = \sum_{i=1}^n (e_i/d_i)^2 \quad 4.2(vii)$$

with respect to each x parameter. The factor S:

$$S = 100 (F/n)^{\frac{1}{2}} \quad 4.2(viii)$$

where N is the number of equations, gives a measure of the average percentage deviation from the ideal, simultaneous, situation.

As has been found earlier, and confirming the results of Section 2.8, the solution is prone to drift, i.e. substantial variation in radii whilst the fit improves only slightly. This is the case even if the more obviously 'covalent' salts are omitted from consideration.

The best fit obtained from 47 of the equations (omitting some salts) has an S value of 4.5%, these radii are given in Table 4.2(iii). As can be seen the anion radii have increased from the values previously assigned whilst those for the cation have decreased, as a result of

Table 4.2(iii) Basic radii obtained by least squares fit ( $\text{\AA}$ ).

Ion	$\bar{r}$	Ion	$\bar{r}$
$\text{Li}^+$	0.224	$\text{Be}^{2+}$	0 *
$\text{Na}^+$	0.782	$\text{Mg}^{2+}$	0.296
$\text{K}^+$	1.103	$\text{Ca}^{2+}$	0.860
$\text{Rb}^+$	1.219	$\text{Sr}^{2+}$	1.039
$\text{Cs}^+$	1.390	$\text{Ba}^{2+}$	1.233
$\text{F}^-$	1.216	$\text{O}^{2-}$	1.645
$\text{Cl}^-$	1.579	$\text{S}^{2-}$	1.938
$\text{Br}^-$	1.695	$\text{Se}^{2-}$	2.021
$\text{I}^-$	1.870	$\text{Te}^{2-}$	2.159

\* least squares fit gives a negative value, zero is assured

Results

the drifting solution. If all compounds are considered this effect is more pronounced. The 'degree of fit' for this 'optimum' solution is only marginally better than a somewhat less rigorous method of assignment used below, which has the advantage of producing more reasonably comparative radii.

The approach thought most appropriate is to accept the earlier results for alkali metal and halide ions and to estimate values for the other ions by consideration of a few chosen salts. The basic radii for the chalcogenide ions are obtained via the  $M_2X$  salts, for calcium, strontium and barium from the  $MX_2$  salts and magnesium from the chalcogenide ion results and the  $MgX$  salts. The radii estimated in this fashion are given in Table 4.2(iv) where they are compared to the values obtained by Huggins and Sakamoto (1957) (whose values are higher for cations and lower for anions).

For the alkali halides, as part of the basic radii studies, lattice energies were computed, which agreed with the results of other workers. However lattice energies from other salts will not be quoted here, the values suffer from high and differing  $\Delta_1$  values (see Section 1), as do all values calculated for these salts with the ionic

#### Results

Table 4.2(iv) Finally assigned and literature basic radii for some monatomic ions ( $\text{\AA}$ ).

Ion	$\rho(\text{\AA}) - \bar{r}(\text{HS})^*$ 0.3333	$\bar{r}(\text{HS})^*$ 0.40	$\bar{r}(\text{this work})$ 0.345
$\text{Li}^+$	-	-	0.456
$\text{Na}^+$	-	-	0.875
$\text{K}^+$	-	-	1.190
$\text{Rb}^+$	-	-	1.320
$\text{Cs}^+$	-	-	1.467
$\text{Be}^{2+}$	0.52	0.75	0.0
$\text{Mg}^{2+}$	0.93	1.10	0.748
$\text{Ca}^{2+}$	1.17	1.31	1.142
$\text{Sr}^{2+}$	1.31	1.44	1.266
$\text{Ba}^{2+}$	1.46	1.58	1.424
$\text{F}^-$	-	-	1.119
$\text{Cl}^-$	-	-	1.506
$\text{Br}^-$	-	-	1.626
$\text{I}^-$	-	-	1.814
$\text{O}^{2-}$	1.35	1.27	1.512
$\text{S}^{2-}$	1.69	1.62	1.827
$\text{Se}^{2-}$	1.78	1.71	1.936
$\text{Te}^{2-}$	1.93	1.86	2.108

\* HS - Huggins and Sakamoto (1957)

#### Results

assumption. The lattice energies are not the object of the calculations and a lengthy study (as any would need to be) concerning them would not be appropriate at this point in time. The new method has not been developed for application to these systems.

Two other common cations are encountered in many studies on complex anions. The ammonium ion in many instances can be considered as spherical, due to free rotation, or has to be assumed so due to the lack of other data. A basic radius for the ammonium ion is computed by considering the structures of the ammonium halides given in Wyckoff (1965). The results are given in Table 4.2(v), assuming the dispersion energy data in Table 4.2(i), and the assignment:

$$r_{\text{NH}_4^+} = 1.265 \text{ \AA} \quad 4.2(\text{ix})$$

is made.

The thallium ion causes problems as to assignment of a spherical ion radius due to its high polarisability, hence its inclination to distort from spherical symmetry. The result given in Jenkins and Pratt (1977a) is felt to be the best estimate possible at this stage, as it is

#### Results

Table 4.2(v) Ammonium halide results giving the basic radius of the ammonium ion ( $\text{kJ.mol}^{-1}$ ).

Salt	$U_{\text{ELEC}}$	$U_{\text{dd}}$	$U_{\text{qd}}$	$U_{\text{POT}}$	$\bar{r}_{\text{NH}_4} + (8)$
$\text{NH}_4\text{F}^*$	855	31	4	753	1.326
$\text{NH}_4\text{Cl}$	730	46	5	677	1.265
$\text{NH}_4\text{Br}$	697	47	5	651	1.265
$\text{NH}_4\text{I}$	669	37	4	624	1.302

\* combination of the different results from the two derivatives

Results



derived from the cubic chloride salt. The similar sizes of these ions should keep any distortion to a minimum.

Other monatomic ions could be assigned basic radii but it is felt that assignments should be made when appropriate for the somewhat less common ions when the particular environment can be chosen to suit the problem.

From the contents of this section it can be seen that the evaluation of basic radii is far from being an exact process. This is so for two major reasons, one the balancing of the anion and cation radii and two, the differing environments from salt to salt (e.g. differing coordination numbers). Due to these factors, although ideally the basic radius can be considered an 'ion property', it is used as such in this work with great caution. The fact that the method evaluates one radius per salt, coupled with the balancing condition, means lack of accuracy in initial basic radii hardly affects the results obtained by the method (see Section 2.8).

#### 4.3 The Cyanide Ion

The cyanide ion has received much attention as far as lattice energy calculation over the years. This is mainly

#### Results

due to the fact that the alkali metal salts (excluding lithium) have the sodium or cesium chloride structure at room temperature making the necessary calculations simple. The low-temperature orthorhombic forms of sodium and potassium cyanide however were treated only fairly recently (Ladd (1969)). The structures of further pleomorphs of potassium cyanide have recently been obtained (Decker, Beyerlein, Rault and Worlton (1974)) and these, along with ammonium cyanide, have not been treated prior to this work.

As a part of this research three papers concerning lattice energy calculations involving the cyanide ion have been published (Jenkins and Pratt (1976a, 1977b) and Jenkins, Pratt and Waddington (1977)). The first of these papers (Jenkins and Pratt (1976a)) dealt with a study of the cubic and orthorhombic pleomorphs of sodium and potassium cyanide, using the old method of calculation (i.e. no minimisation involved) where the basic radii used for the anion had to be estimated. The second paper (Jenkins, Pratt and Waddington (1977)) includes the salts considered in the first together with lithium, rubidium and cesium cyanides, and also an experimental determination of the enthalpy of solution of lithium cyanide. These calculations also use the older method of

#### Results

calculation. Both of these two papers involve the necessity of choosing ionic polarisabilities; for the cations they were taken from the work of Pauling (1927) whilst that for the cyanide ion itself was taken from Tessman, Kahn and Shockley (1957). This inconsistency leads to only small errors in the dispersion energies, terms which are small in themselves for these salts, and so does not affect the results of these papers greatly, but the situation is improved by taking all polarisabilities from Tessman et al. Such parameters are adopted throughout later work on the cyanide ion described below.

The third paper (Jenkins and Pratt (1977b)) considers the cubic alkali metal cyanides by the new minimisation approach. The calculations were carried out at a stage in the research when the new method had only been developed for cubic systems, hence the exclusion of other salts and structures. The results for the lattice energies produced in this study were very close to, but consistently higher than, those of the earlier studies. This arises due to a slight overestimate in the basic radius of the cyanide ion in this early work (coupled with the dispersion energy error alluded to above).

## Results

The obvious 'next step' in such studies is the application of the new method to the non-cubic pleomorphs, along with the inclusion of later values for thermodynamic parameters. The results for the cubic salts are taken from Jenkins and Pratt (1977b), those corresponding to the cell constants taken from Wyckoff (1965). The cubic salts have cyanide ions which are freely rotating (Elliott and Hastings (1961)) and hence no distribution of charge in the ion can be taken into consideration, a point charge model is taken. At lower temperatures, or higher pressures, this rotation is restricted and the pleomorphs can be considered as having a dipolar cyanide ion, the lattice energy being computed as a function of the charge distribution in this ion. The single negative charge is considered as being partially located on the carbon ( $q_C$ ) and partially on the nitrogen ( $q_N$ ) atoms, so:

$$q_C + q_N = -1 \quad 4.3(1)$$

Structures which have been reported and which have non-rotating cyanide ions are the orthorhombic structures of sodium and potassium cyanide(II) (Verweel and Bijvoet (1938) and Bijvoet and Lely (1940)) and the orthorhombic room temperature structure of lithium cyanide (Lely and

#### Results

dijveot (1942)), all considered in the early work. Also the tetragonal structure of ammonium cyanide (Lely and dijveot (1944)) and the high pressure monoclinic structure of potassium cyanide(IV) (Decker, Beverlein, Rault and Worlton (1974)) show non-rotating cyanide ions. Decker et al also report a cubic structure for the high pressure form of potassium cyanide(III) in which the cyanide ions, although not freely rotating, are randomly orientated along the (111) directions. This structure is treated in this study as having spherical cyanide ions. The space group and cell constants of these structures are given in Table 4.3(i).

The results for lithium cyanide given by Jenkins, Pratt and Waddington (1977) indicate a charge (absolute) on the nitrogen too large to be consistent with all other indications (see later), this is confirmed by calculations using the new method. The crystal structure of lithium cyanide was determined in 1942 on a 'grey solid'. The solution calorimetry work, carried out in 1975 as part of this research, used a pure white solid, indicating that Lely and dijveot had an impure sample. (Lithium cyanide is very air sensitive, see the notes on the solution work.) Consequently the results for lithium cyanide are excluded from this work as they cannot be considered accurate.

#### Results

Table 4.3(i) Details of the unit cells of KCN crystals.

KCN	space group	z	Cell constants (Å)				Distance C-N (Å)
			a	b	c		
KCN	P6 <sub>3</sub> m	4	6.52	8.73	3.73	90°	1.142
K <sub>2</sub> CN(I)	Fm3m	4	5.993	(=a)	(=a)	90°	-
K <sub>2</sub> CN(II)	Im2m	2	3.774	4.719	5.640	90°	1.049
KCN(I)	Fm3m	4	6.527	(=a)	(=a)	90°	-
KCN(II)	Im2m	2	4.24	5.14	6.16	90°	1.072
KCN(III)	Fm3m	1	3.908	(=a)	(=a)	90°	-
KCN(IV)	C <sub>2</sub> v	2	5.531	5.219	3.743	94.4°	1.055
LiCN	Fm3m	4	6.92	(=a)	(=a)	90°	-
CSN	Pm3m	1	4.25	(=a)	(=a)	90°	-
NH <sub>4</sub> CN*	P4/mcm	2	4.16	(=a)	7.64	90°	1.094

\* carbon and nitrogen positions not distinguished, but are equivalent.

All parameters are the same as used in the earlier studies except that the ionic polarisabilities of Tessman, Kahn and Shockley (1953) are used throughout and the basic radii are selected from Jenkins and Pratt (1976b), corresponding to these polarisabilities. All that is left to describe now is the repulsion model. For the cubic salts considered earlier this was the assumption of spherical symmetry due to rotation. There are two clear possibilities for models of a non-rotating cyanide ion which are applicable within the new method. Firstly a spherical ion model, as for the cubic salts, this will obviously exaggerate the size of the envelope at the centre of the ion whilst not being sufficient at the extremities. The second possibility is one of two equal spheres centered on the atoms and is the more immediately appealing and if the atoms were 'singly bonded' (large electron density away from the bond - such as in chlorine) it would probably be a reasonable model. However for the cyanide ion this model does not allow for the large electron density between the atoms and greatly exaggerates the electron density at the ends of the ion.

If the non-availability of an appropriate model was the only problem in this case we would still probably be able to produce reasonable values for lattice energies by

## Results

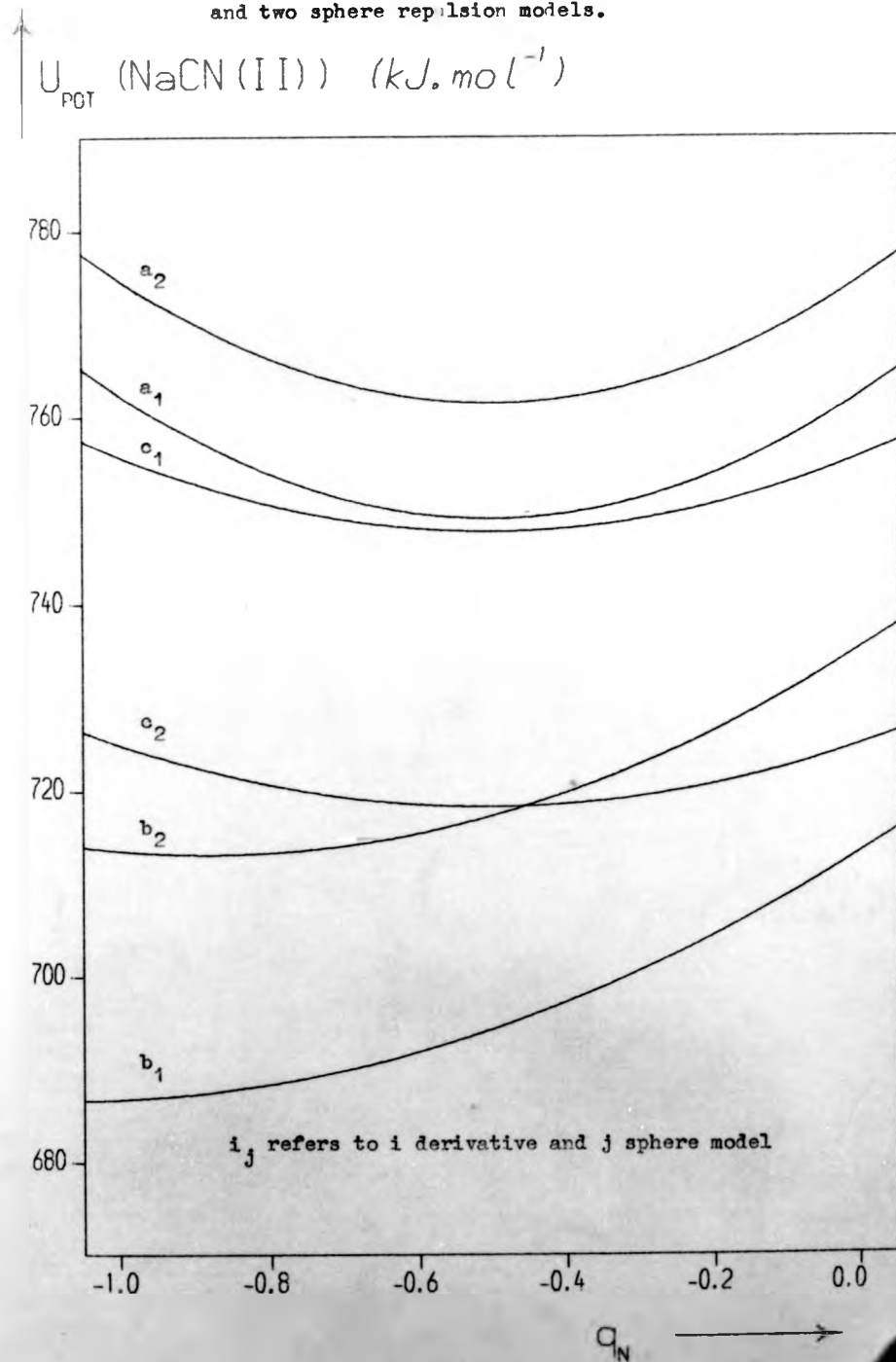
use of the flexibility imposed by the minimisation. However the major problem, most obvious in the case of the two bimolecular orthorhombic salts which are discussed as an example, is the total anisotropy of the ion brought about by the differing interactions: along the a direction we have solely cyanide-cyanide 'side on' interactions, along the b direction cyanide-cyanide 'end on' interactions and along the c direction sodium-cyanide ('side on') interactions. So no matter which model is taken very different radii are produced by the minimisation in each different direction. The cyanide ion loses even cylindrical symmetry because of its environment. The results for the lattice energy of  $\text{NaCN(II)}$  as a function of the charge distribution for the two models, and minimisation in the three directions, are shown in Figure 4.3(i). This figure shows how the anisotropy prevents meaningful intersections, and hence the securing of a value for the lattice energy and a charge distribution.

The exceptional anisotropy forces us to adopt a different approach for this ion. The true repulsion envelope will be closely approximated by a solid ellipsoid with three major axes of different lengths. Consequently an approach similar to that used by Jenkins, Dixon and

## Results



Figure 4.3(i) Lattice energy of sodium cyanide for the one and two sphere repulsion models.



Jaddington (1972), in treating the bifluoride ion as an ellipsoid of revolution, must be adopted. They had two different major axes which they had to estimate. In this case we have three but the results of the minimisation using the spherical anion model give the three axes for each value of the charge distribution. From the lengths of the three major axes we can assign a value to use for the basic radius for each interaction by combining them with the knowledge of the direction of the interaction relative to the orientation of the ellipsoid.

All the structures considered here, except that for potassium cyanide(IV), are rectangular, and this can be assumed as such for these purposes. The equation of the ellipsoid is:

$$\frac{x^2}{r_a^2} + \frac{y^2}{r_b^2} + \frac{z^2}{r_c^2} = 1 \quad 4.3(11)$$

(if it is assumed that the centre of the cyanide ion is the origin) where  $r_a$ ,  $r_b$  and  $r_c$  are the three basic radii obtained from our 'spherical anion' model and  $x$ ,  $y$  and  $z$  are rectangular coordinates. The direction of the interaction being considered can be parameterised by:

$$y = ux, \quad z = vx \quad 4.3(11i)$$

#### Results

where  $u$  and  $v$  are known parameters. If the coordinates of the point of intersection between the above line and the ellipsoid are  $(x_I, y_I, z_I)$  then the 'basic radius' required ( $\bar{r}_{CN}$ ) is:

$$\bar{r}_{CN}^2 = x_I^2 + y_I^2 + z_I^2 \quad 4.3(iv)$$

and so:

$$\bar{r}_{CN}^2 = x_I^2(1 + u^2 + v^2) \quad 4.3(v)$$

Also:

$$\frac{x_I^2}{\bar{r}_a^2} + \frac{u^2 x_I^2}{\bar{r}_b^2} + \frac{v^2 x_I^2}{\bar{r}_c^2} = 1 \quad 4.3(vi)$$

consequently;

$$\bar{r}_{CN}^2 = \frac{\bar{r}_a^2 \bar{r}_b^2 \bar{r}_c^2 (1 + u^2 + v^2)}{(\bar{r}_b^2 \bar{r}_c^2 + u^2 \bar{r}_a^2 \bar{r}_c^2 + v^2 \bar{r}_a^2 \bar{r}_b^2)} \quad 4.3(vii)$$

The repulsive interactions included (excluding

## Results

cation-cation which are straightforward) for each crystal structure are listed in Table 4.3(ii). Only the major interactions are included to facilitate calculation. The calculations for potassium cyanide (IV) are only approximate (due to the non-rectangular structure) but no appreciable error is believed to be introduced.

This approach has the disadvantage that only one curve of lattice energy versus charge distribution is now produced for each structure rather than three (or two, as for ammonium cyanide). However this is unavoidable. The curve is obtained, at each value of the charge distribution, by taking the values for the three major axes of the basic ellipsoid from the results for the 'spherical anion' model and for each interaction computing the actual basic 'distance' ( $\bar{r}_{CN}$ ) from Equation 4.3(vii) and hence the repulsive energy of the interaction. In all the structures the cyanide ions are parallel and so for the cyanide-cyanide repulsions the two basic 'distances' involved are equal.

The resultant curve of the lattice energy versus charge distribution for sodium cyanide(II) is shown in Figure 4.3(ii), those for potassium cyanide(II) and (IV) in Figure 4.3(iii) and that for ammonium cyanide in Figure

Figure 4.3(ii) Lattice energy of the pleomorphs of sodium cyanide  
for the ellipsoidal repulsion model.

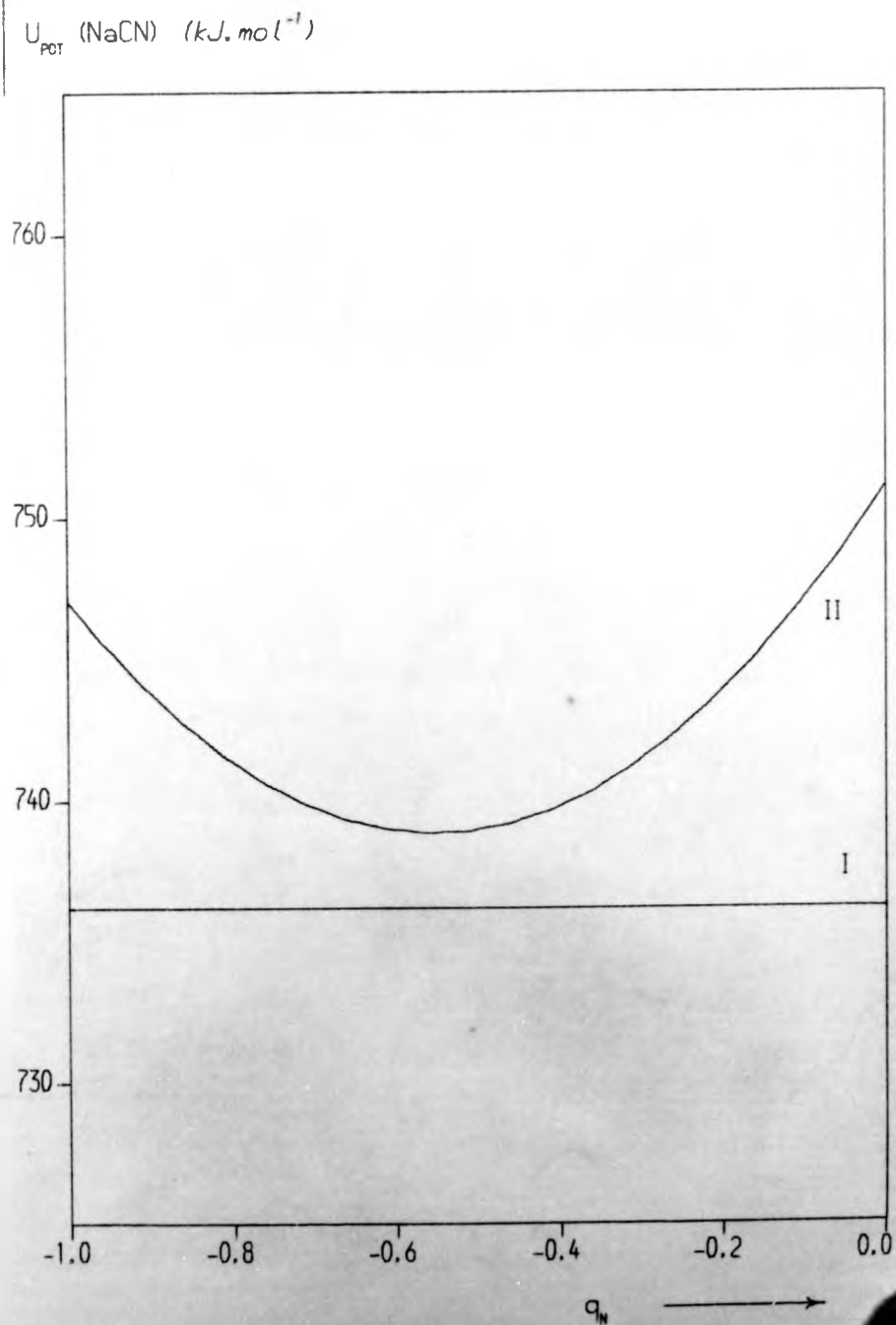


Figure 4.3(iii) Lattice energy of the pleomorphs of potassium cyanide for the ellipsoidal repulsion model.

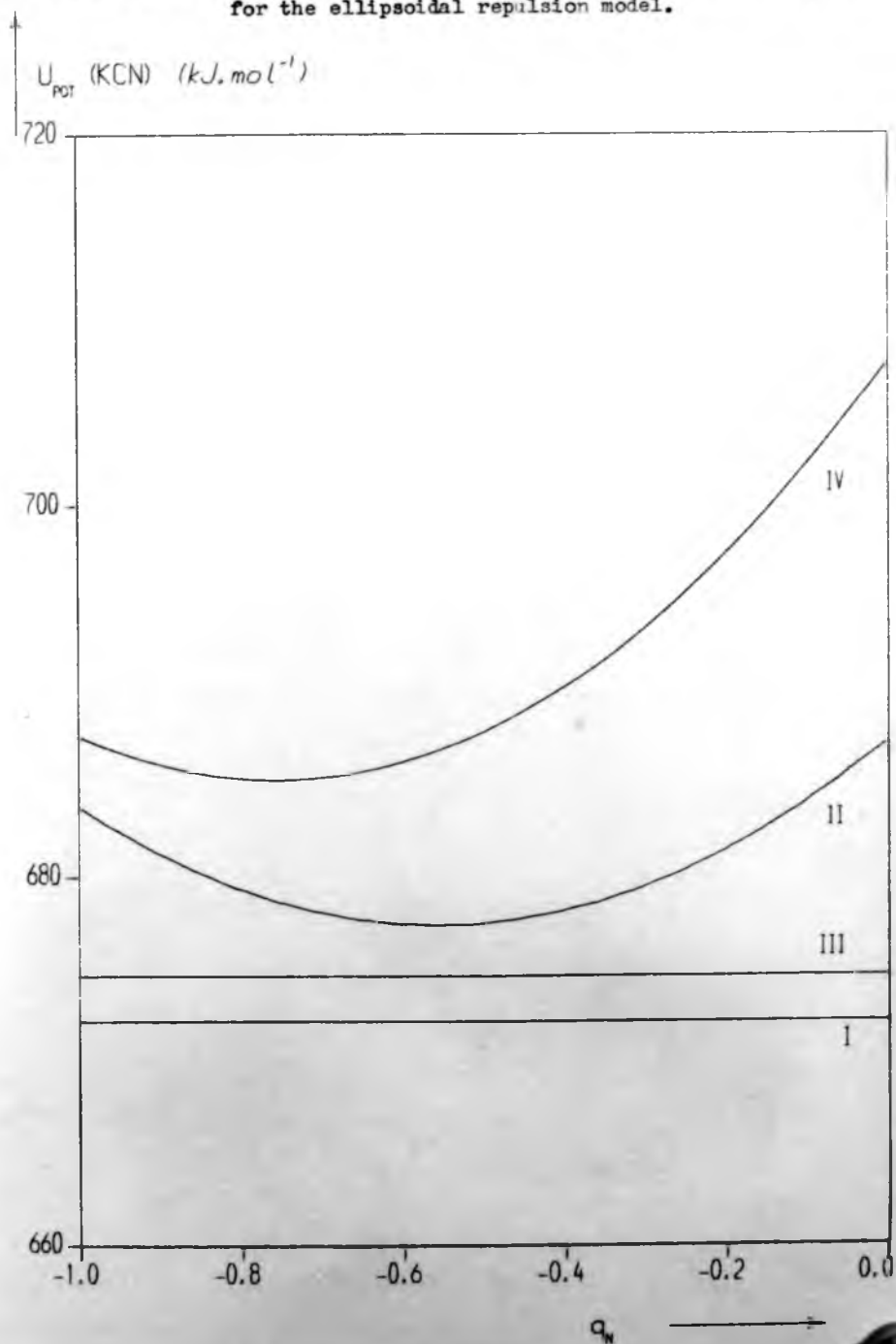


Table 4.3(ii) Cation-anion and anion-anion contacts in some cyanide crystals.

Closest Interactions				
Salt	Cation relative to cyanide ion	No.	Cyanide relative to cyanide ion	No.
NaCN (II)	$(\pm 1/2, \pm 1/2, 0)$	4	$(\pm 1/2, \pm 1/2, \pm 1/2)$	8
	$(0, 0, \pm 1/2)$	2	$(\pm 1, 0, 0)$	2
KCN (II)			$(0, \pm 1, 0)$	2
			$(0, 0, \pm 1)$	2
KCN (IV)	ca. $(\pm 1/2, 0, \pm 1/2)$	4	$(0, 0, \pm 1)$	2
	ca. $(0, \pm 1/2, \pm 1/2)$	4	$(\pm 1/2, \pm 1/2, 0)$	4
$NH_4CN$	$(\pm 1/2, \pm 1/2, \pm 1/4)$	8	$(0, 0, \pm 1/2)$	2
			$(\pm 1, 0, 0)$	2
			$(0, \pm 1, 0)$	2

Results

4.3(iv). Where applicable the appropriate lattice energies for cubic salts with rotating cyanide ions are also shown in these figures.

The results for the Madelung energy ( $U_M$ ) are parameterised by:

$$U_M = \sum_{i=0}^2 A_i q_N^i \quad 4.3(viii)$$

the self energy ( $U_{SE}$ ) by:

$$U_{SE} = \sum_{i=1}^2 B_i q_N^i \quad 4.3(ix)$$

the electrostatic energy ( $U_{ELEC}$ ) by:

$$U_{ELEC} = \sum_{i=0}^2 C_i q_N^i \quad 4.3(x)$$

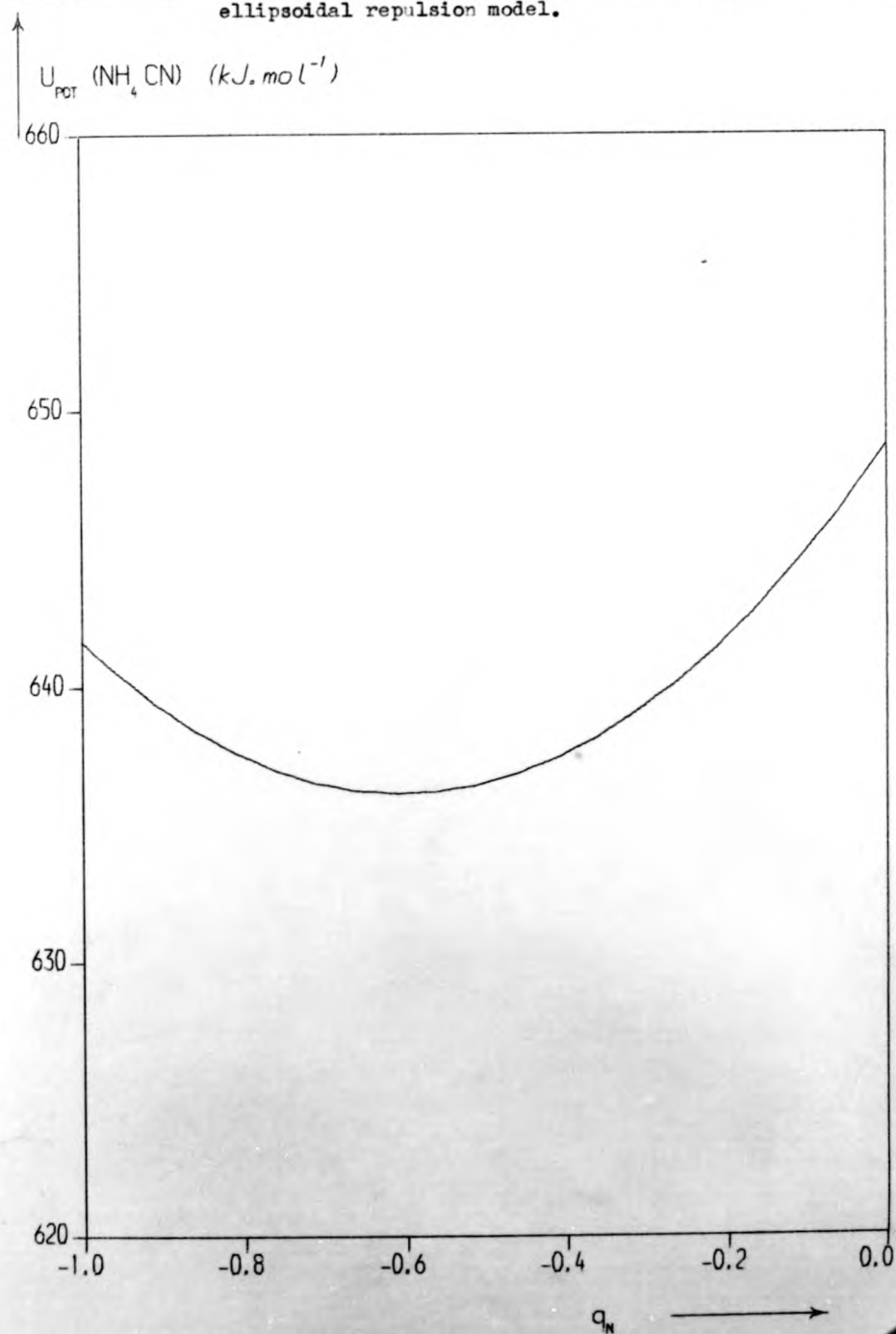
and the cell length derivatives of the electrostatic energy ( $j=a,b,c$ ) by:

$$\left( \frac{\partial U_{ELEC}}{\partial l} \right)_{l=l_0} = \sum_{j=0}^2 D_{ij} q_N^j \quad 4.3(xi)$$

## Results



Figure 4.3(iv) Lattice energy of ammonium cyanide for the ellipsoidal repulsion model.



These values are given in Table 4.3(iii). Along with the dipole-dipole ( $U_{dd}$ ) and dipole-quadrupole ( $U_{qd}$ ) dispersion energies and derivatives, the cation basic radius and the cation-cation repulsion energy ( $U_R^{++}$ ).

The lattice energy results shown in Figures 4.3(ii)-4.3(iv) can be combined on to one graph by consideration of a thermochemical cycle which relates the lattice energy to the enthalpy of formation of the gaseous cyanide ion. The equality produced from this cycle is:

$$\Delta H_f^\circ(CN^-)(g) = U_{POT}(MCN) + \Delta H_f^\circ(MCN)(o) - \Delta H_f^\circ(M^+)(g) + nRT \quad 4.3(xi)$$

where  $n=0$  for monatomic  $M$  and  $n=3/2$  for ammonium.

The most recently available thermochemical data is listed in Table 4.3(iv) and this is combined with the lattice energy results to give the plot of the enthalpy of formation of the gaseous cyanide ion versus the charge on the nitrogen atom given in Figure 4.3(v). Here the plots corresponding to the results for potassium cyanide(III) and (IV) are given as broken lines as they are inaccurate by the unknown amount of their transition enthalpies from the II form.

#### Results

Figure 4.3(v) Enthalpy of formation of the gaseous cyanide ion.

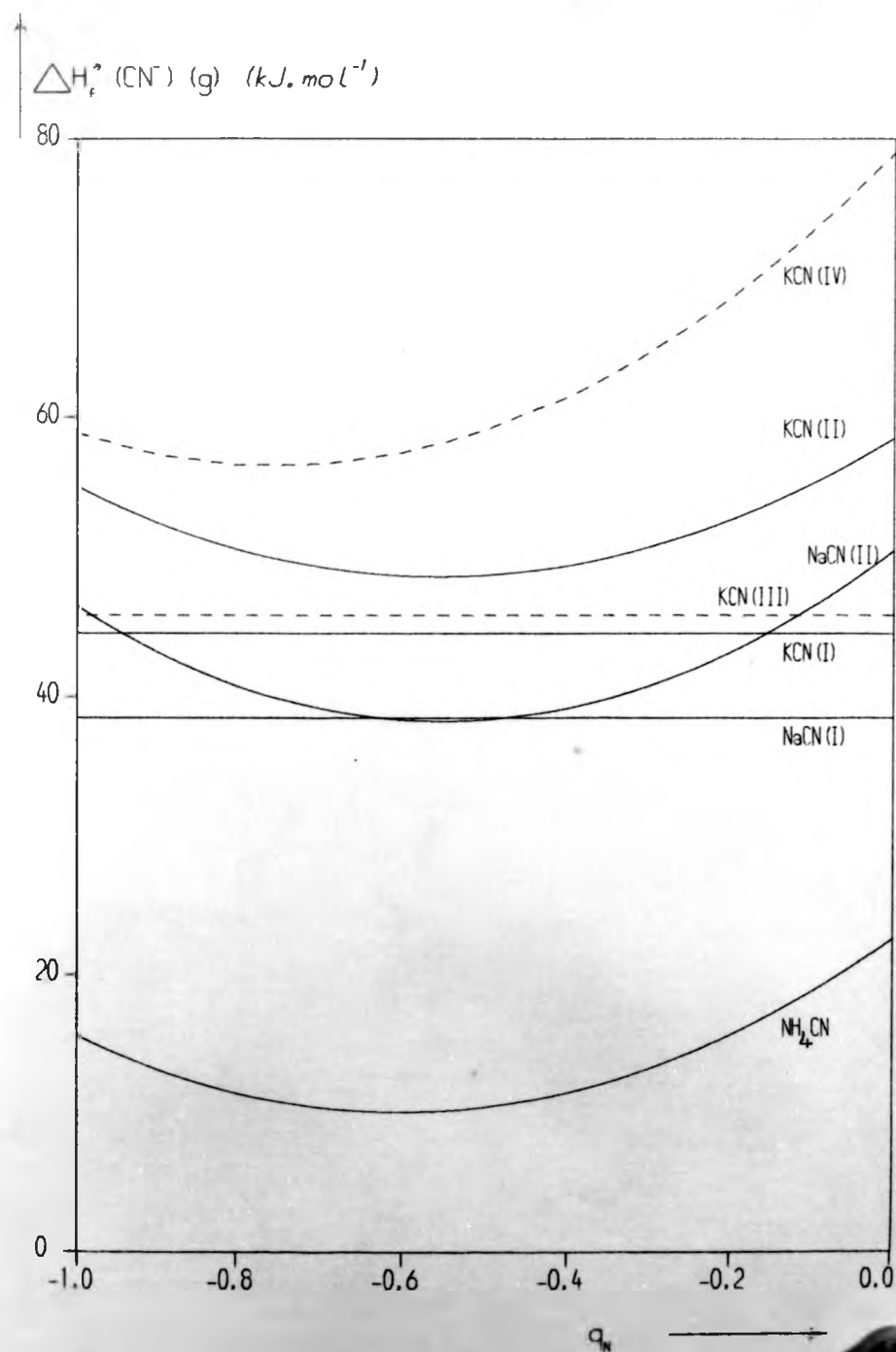


Table 4.3(iii) Intermediate results for cyanide salts  
not treated in Jenkins and Pratt (1977b).

Term	NaCN (II)	KCN (II)	KCN (III)	KCN (IV)	NH <sub>4</sub> CN	Units
A <sub>0</sub>	835.4	759.3	742.6	774.9	711.2	
A <sub>1</sub>	1379.2	1330.5	-	1382.4	1319.9	kJ.mol <sup>-1</sup>
A <sub>2</sub>	1379.2	1330.5	-	1371.4	1319.9	
U <sub>1</sub>	-1326.2	-1287.1	-	-1316.5	-1296.6	kJ.mol <sup>-1</sup>
U <sub>2</sub>	-1326.2	-1287.1	-	-1316.5	-1296.6	
C <sub>0</sub>	835.4	759.3	742.6	774.9	711.2	
C <sub>1</sub>	53.0	43.4	-	65.9	50.3	kJ.mol <sup>-1</sup>
C <sub>2</sub>	53.0	43.4	-	54.9	50.3	
D <sub>a0</sub>	-47.8	-40.7	-195.0	-57.8	-130.7	
D <sub>a1</sub>	0.3	-0.7	-	-3.7	-19.7	kJ.mol <sup>-1</sup>
D <sub>a2</sub>	0.3	-0.7	-	-5.6	-35.4	g <sup>-1</sup>
D <sub>b0</sub>	-72.9	-57.5	-	-57.1	-	
D <sub>b1</sub>	-1.8	-2.4	-	-19.0	-	kJ.mol <sup>-1</sup>
D <sub>b2</sub>	-17.3	-12.8	-	-13.0	-	g <sup>-1</sup>
D <sub>c0</sub>	-55.2	-47.3	-	-52.5	-21.9	
D <sub>c1</sub>	-13.6	-9.7	-	2.4	0.0	kJ.mol <sup>-1</sup>
D <sub>c2</sub>	-13.6	-9.7	-	-15.6	0.0	g <sup>-1</sup>
U <sub>dd</sub>	9.5	14.5	19.2	20.5	21.0	kJ.mol <sup>-1</sup>

continued over

Results

Table 4.3(iii) continued

Term	NaCN (II)	KCN (Ia)	KCN (III)	KCN (IV)	NH <sub>4</sub> CN	Units
$\partial U_{ad}/\partial a$	-4.6	-5.9	-30.3	-7.1	-19.5	
$\partial U_{ad}/\partial b$	-3.8	-5.3	-	-9.2	-	$\text{kJ. mol}^{-1}$
$\partial U_{ad}/\partial c$	-3.8	-5.6	-	-10.9	-5.9	$\text{\AA}^{-1}$
$U_{qd}$	0.5	1.1	1.4	1.5	1.0	$\text{kJ. mol}^{-1}$
$\partial U_{qd}/\partial a$	-0.3	-0.5	-3.0	-0.7	-2.2	
$\partial U_{qd}/\partial b$	-0.2	-0.5	-	-1.9	-	$\text{kJ. mol}^{-1}$
$\partial U_{qd}/\partial c$	-0.3	-0.6	-	-1.1	-0.7	$\text{\AA}^{-1}$
$U_{R}^{++}$	0.5	1.0	3.9	4.2	3.3	$\text{kJ. mol}^{-1}$
$\bar{r}_M$	0.875	1.197	1.197	1.197	1.271	$\text{\AA}$

Results

Table 4.3(iv) Thermochemical data for cyanide salts (in  $\text{kJ}\cdot\text{mol}^{-1}$ ).

MCN	$\Delta_f H^\circ(\text{MCN})(c)$	Source	$\Delta_f H^\circ(M^+)(g)$	Source
NaCN(I)	-97.8	a	609.8	b
NaCN(II)	-90.9	a	609.8	b
KCN(I)	-113.4	a	514.2	b
KCN(II)	-114.6	a+b	514.2	b
$\text{NH}_4\text{CN}$	0.4	c	630.2	d

a) Wagman et al (1976)

b) Stull and Prophet (1971)

c) Wagman et al (1965)

d) Jenkins and Morris (1976)

The results for ammonium cyanide are somewhat at variance with the others. This is possibly due to an error in the enthalpy of formation of the salt (the United States National Bureau of Standards quote a value in Technical Note 270.1 (Wagman et al (1965)) and exclude it in the later 270.3 (Wagman et al (1968))) or some interionic hydrogen bonding. The results are excluded from the later considerations because of this uncertainty.

In order to proceed to the assignment of lattice energies and thermochemical data it is necessary to have a measure of the charge distribution in the cyanide ion. Normally we would expect to be able to assign the charge distribution from one of the plots already produced, however due to the anisotropy of the system we have been restricted in the amount of lattice energy data that can be obtained, hence no intersection points and no possibility of assignment. It is necessary therefore to make some estimate of the charge distribution and it is fortunate that the ion is of a simple nature.

Two quantum mechanical estimates of the charge on the nitrogen atom seem to agree well; Demynck, Veillard and Vinot (1971) find  $q_N = -0.57$  and Hillier and Sanders (1972) find  $q_N = -0.59$ . These also agree with the estimate from

#### Results

the early work in this research (when the lithium cyanide results are omitted) of  $-0.575$ . This value is about what would be expected from simple electronegativity grounds, the nitrogen atom having only a slightly higher electronegativity than the carbon atom. So I have decided to use an average of the above two quantum mechanical estimates here ( $q_N = -0.58$ ). The low variation of lattice energy with charge shown by all the salts considered is a bonus in the sense that any error incurred by this estimate must be small.

Another indication that the charge distribution is appreciably correct is that it is shown as a turning point in the curves obtained. With the low variation in charge and the approximately pure parabolic nature of the curves one could not have one intersection without a second, this would indicate two possible states and is an unreal situation. The ideal arrangement of the curves must then be that the parabolic curves should touch the straight lines, so indicating that the turning point of the parabolic curves should show an estimate for the charge distribution in the cyanide ion.

The results, assuming a charge distribution corresponding to  $q_N = -0.58$ , are:

#### Results



$$U_{\text{POT}}(\text{NaCN(II)}) = 739 \text{ kJ.mol}^{-1} \quad 4.3(\text{xiii})$$

$$U_{\text{POT}}(\text{KCN(II)}) = 677 \text{ kJ.mol}^{-1} \quad 4.3(\text{xiv})$$

$$U_{\text{POT}}(\text{KCN(III)}) = 675 \text{ kJ.mol}^{-1} \quad 4.3(\text{xv})$$

$$U_{\text{POT}}(\text{KCN(IV)}) = 687 \text{ kJ.mol}^{-1} \quad 4.3(\text{xvi})$$

$$U_{\text{POT}}(\text{TH}_4\text{CN}) = 636 \text{ kJ.mol}^{-1} \quad 4.3(\text{xvii})$$

$$\Delta H_f^\circ(\text{CN}^-)(\text{g}) = 43 \pm 5 \text{ kJ.mol}^{-1} \quad 4.3(\text{xviii})$$

The results for the room temperature cubic salts are quoted in Jenkins and Pratt (1977b). The deviation quoted in Equation 4.3(xviii) is a standard deviation of the average of the four values obtained from the sodium and potassium cyanide (I) and (II) salts and **not** a measure of the absolute error. The value of the lattice energy of potassium cyanide(IV) seems slightly high in relation to the other polymorphs.

Other results that can be extracted are.

(a) There appears to be no correlation between the radii produced from the calculations on different salts. Presumably due to the differing environments of the cyanide ions and the large 'cloud' of electron density

## Results

around the ion. The radii found for the high pressure structures are generally lower than for the others.

(b) The hydration enthalpy of the cyanide ion is given by:

$$\Delta H_{\text{hyd}}^{\circ}(\text{CN}^{-})(g) = \Delta H_{\text{f}}^{\circ}(\text{H}^{+})(\text{aq}) + \Delta H_{\text{f}}^{\circ}(\text{CN}^{-})(\text{aq}) - \Delta H_{\text{f}}^{\circ}(\text{H}^{+})(g) - \Delta H_{\text{f}}^{\circ}(\text{CN}^{-})(g) - \Delta H_{\text{hyd}}^{\circ}(\text{H}^{+})(g) \quad 4.3(\text{xx})$$

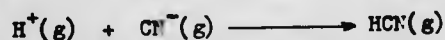
and taking  $\Delta H_{\text{f}}^{\circ}(\text{H}^{+})(\text{aq}) = 0$  (convention),  $\Delta H_{\text{f}}^{\circ}(\text{CN}^{-})(\text{aq}) = 151.6 \text{ kJ.mol}^{-1}$  (Wajman et al (1968)),  $\Delta H_{\text{f}}^{\circ}(\text{H}^{+})(g) = 1536.2 \text{ kJ.mol}^{-1}$  (Wajman et al (1968)) and  $\Delta H_{\text{hyd}}^{\circ}(\text{H}^{+})(g) = 0$  we obtain the conventional hydration enthalpy:

$$\Delta H_{\text{conv hyd}}^{\circ}(\text{CN}^{-})(g) = -1429 \text{ kJ.mol}^{-1} \quad 4.3(\text{xx})$$

Using  $\Delta H_{\text{hyd}}^{\circ}(\text{H}^{+})(g) = -1100.6 \text{ kJ.mol}^{-1}$  (Jenkins and Morris (1976)) we obtain the absolute hydration enthalpy:

$$\Delta H_{\text{abs hyd}}^{\circ}(\text{CN}^{-})(g) = -328 \text{ kJ.mol}^{-1} \quad 4.3(\text{xxd})$$

(c) The process corresponding to the proton affinity of the cyanide ion,  $\Delta H_1$ , is:



#### Results

Using the data (Kagman et al (1968))  $\Delta H_f^\circ(\text{HCN})(g) = 135.1$  and  $\Delta H_f^\circ(\text{H}^+)(g) = 1536.2 \text{ kJ.mol}^{-1}$  along with the result for the cyanide ion we estimate:

$$\Delta H_1 = -1444 \text{ kJ.mol}^{-1} \quad 4.3(\text{xodi})$$

(d) The electron affinity of the cyanide radical ( $\text{EA}(\text{CN}^\bullet)$ ) is given by:

$$-\text{EA}(\text{CN}^\bullet) = \Delta H_f^\circ(\text{CN}^-)(g) - \Delta H_f^\circ(\text{CN}^\bullet)(g) + \frac{5}{2} RT \quad 4.3(\text{xodi})$$

Using the data  $\Delta H_f^\circ(\text{CN}^\bullet)(g) = 456.1 \text{ kJ.mol}^{-1}$  (Kagman et al (1968)) we obtain:

$$\text{EA}(\text{CN}^\bullet) = 407 \text{ kJ.mol}^{-1} \text{ or } 4.22 \text{ eV} \quad 4.3(\text{xodi})$$

The results in (b)-(d) are all similar to those obtained in the earlier work, where they are compared to the literature values.

The cyanide ion is unique in this study in that the minimisation fails to yield the wealth of information which usually enables the evaluation of the unknown

## Results

parameters. However it does provide a way of treating non-spherical ions (or ions which cannot be approximated by arrays of identical spheres) much more accurately than in previous methods. The agreement with the results from the older method is a testament to the 'accuracy' of the basic radii estimates made in that work.

#### **4.4 The Azide Ion**

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A published part of this research programme (Jenkins and Pratt (1977c)) is the application of the first stage of the Jenkins and Waddington approach (see Section 2.5) to the sodium (trigonal pleomorph), potassium, rubidium, cesium and thallium azide salts, and a comparison between this method of calculating lattice energies and the one which considers the azide ion as an ellipsoid of revolution, used by Dixon, Jenkins and Waddington (1971). Since that work the new method has been quantified and it is now possible to apply this to all the above salts, plus some others not previously considered.

The use of a simple Huggins and Mayer potential combined with the consideration of the azide ion as an ellipsoid suffers from two major faults. The absence of an energy minimisation procedure and the exaggeration of

#### **Results**

the repulsion contribution of the central nitrogen atom of the ion. The Jenkins and Waddington equation removes both of these objections but limits the form of the repulsion energy to that of a **single** exponential term, this results in a certain inflexibility in the calculations. The new method proposed earlier satisfies all the above objections. It should be noted however that all three methods have produced quite similar results.

Very recently a collection of reviews concerning the azide ion have been published. Two of these reviews (Choi (1977) and Gora, Downs, Kenney and Sharma (1977)) contain studies of direct importance to the lattice energy studies to be reported. Choi gives a review of the crystal structures of metal azides. Gora et al give a compilation of the thermochemistry of the metal azides. Both workers provide valuable experimental data for these studies.

Crystal structures are selected for consideration from Gora's work if they are completely resolved and contain symmetrical, linear azide ions. All the divalent salts quoted do not fill this last criterion. The azide salts selected have their unit cell details listed in Table 4.4(i). Some points concerning these structures are made below.

#### Results

Table 4.4(i) Details of the unit cells of azide crystals.

M <sub>3</sub>	Space group	Z	Cell constants (Å)			Dist. N-N(Å)	Ref
			a	b	c		
LiN <sub>3</sub>	C2/m	2	5.627	3.319	4.979	107.4°	1.162 1
NaN <sub>3</sub> (α)	C2/m	2	6.211	3.658	5.373	108.43°	1.168 1
NaN <sub>3</sub> (β)*	P3n	3	3.646	(=a)	15.213	90°	1.162 1, 7
RbN <sub>3</sub>	I4/mcm	4	6.1129	(=a)	7.0743	90°	1.174 2, 3
RbN <sub>3</sub>	I4/mcm	4	6.3096	(=a)	7.5188	90°	1.173 2, 3
CsN <sub>3</sub>	I4/mcm	4	6.5412	(=a)	8.0908	90°	1.173 3
NH <sub>4</sub> N <sub>3</sub> †	Pman	4	8.937	8.642	3.870	90°	1.170 1.157 4
TlN <sub>3</sub>	I4/mcm	4	6.208	(=a)	7.355	90°	1.165 2
AN <sub>3</sub>	Ibam	4	5.6170	5.9146	5.0757	90°	1.180 5, 6
CuN <sub>3</sub>	I4/a	8	8.65	(=a)	5.5°	90°	1.173 7

\* neglecting any orientation disorder of the anion

† atomic coordinates incorrectly quoted by Choi(1977)

1. Fringle and Noakes (1968)
2. Choi and Prince (1976)
3. Muller (1972)
4. Frevel (1936)
5. Pfeiffer (1948)
6. Marr and Stanford Jnr. (1962)
7. Wilsdorf (1948)

## Results

(a) The structures for lithium azide, the monoclinic low temperature form of sodium, ammonium, silver and copper(I) azides are considered for the first time.

(b) The room temperature trigonal structure of sodium azide has been reported (Choi and Prince (1976)) as having some disorder amongst the orientation of the azide ions. As in the previous studies complete order is however assumed.

(c) The tetragonal forms of potassium, rubidium, cesium and thallium azides are here used with slightly different azide ion bond lengths from those in the previous study.

(d) The atomic coordinates associated with the structure for ammonium azide are incorrectly quoted by Choi (1977), they are correct in Wyckoff (1965).

(e) Wyckoff (1965) reports the likelihood of hydrogen bonding in ammonium azide, using the crystal structure as evidence.

(f) Some of the bond lengths quoted by Choi are incorrect.

If we denote the charge on the central nitrogen atom of the azide ion by  $q_N$  and that on the terminal nitrogens by  $q_T$ , then considering a distribution of charge between the atoms:

$$q_N + 2 q_T = -1 \quad 4.4(1)$$

## Results

We can parameterise the electrostatic energy and its cell length derivatives as quadratic functions of the charge on the terminal nitrogen atoms. The results are given in Tables 4.4(ii) and 4.4(iii) using symbols exactly analogous to Equations 4.3(viii)-4.3(xi) used in consideration of the cyanide ion.

The dispersion energies, and derivatives, are calculated using cation polarisabilities from Pirenne and Kartheuser (1964) whilst the calculations in Jenkins and Pratt (1977c) use the values of Tessman, Kahn and Shockley (1953). This cation set was chosen for use with the anion polarisability taken from Frech and Decius (1969) as they appear to use cation values from Pirenne and Kartheuser. The only salt for which this makes a large difference in results is the thallium salt, see later. The cation characteristic energies were taken as 90% of the second ionisation potential of the metals whilst that for the anion was taken from the work of Archibald and Sabin (1971). All electron numbers were taken as eight, apart from lithium (two) and thallium (eleven - Alcock and Jenkins (1974)). The results for the dispersion energies and cell length derivatives are given in Tables 4.4(ii)-4.4(iii).

#### Results



Table 4.4(ii) Intermediate results for lithium, sodium, potassium and rubidium azides.

Term	LiN <sub>3</sub>	NaN <sub>3</sub> (α)	NaN <sub>3</sub> (β)	KN <sub>3</sub>	RbN <sub>3</sub>	Units
A <sub>0</sub>	659.4	632.0	630.0	675.0	653.8	
A <sub>1</sub>	1985.4	2084.6	2085.0	2343.2	2351.9	kJ.mol <sup>-1</sup>
A <sub>2</sub>	4069.7	4092.4	4101.1	4177.4	4175.2	
B <sub>1</sub>	-2390.4	-2377.8	-2390.7	-2366.8	-2367.9	kJ.mol <sup>-1</sup>
B <sub>2</sub>	-4183.2	-4164.6	-4183.7	-4141.9	-4143.9	
C <sub>0</sub>	659.4	632.0	630.0	675.0	653.8	
C <sub>1</sub>	-405.0	-295.2	-305.6	-23.7	-16.1	kJ.mol <sup>-1</sup>
C <sub>2</sub>	-113.5	-72.2	-82.5	35.5	31.3	
D <sub>a0</sub>	38.3	25.1	71.6	-112.1	-103.4	
D <sub>a1</sub>	158.8	111.2	351.0	-56.9	-49.7	kJ.mol <sup>-1</sup>
D <sub>a2</sub>	46.0	27.0	106.7	-42.2	-34.6	q <sup>-1</sup>
D <sub>b0</sub>	51.8	31.4	-	-	-	
D <sub>b1</sub>	233.0	156.7	-	-	-	kJ.mol <sup>-1</sup>
D <sub>b2</sub>	82.5	50.0	-	-	-	q <sup>-1</sup>
D <sub>c0</sub>	-210.2	-169.7	-58.6	1.5	-2.7	
D <sub>c1</sub>	-117.4	-88.1	-30.5	46.8	38.8	kJ.mol <sup>-1</sup>
D <sub>c2</sub>	-8.1	-5.6	-2.0	9.4	6.8	q <sup>-1</sup>
U <sub>dd</sub>	35.1	27.2	26.2	34.0	35.4	kJ.mol <sup>-1</sup>

continued over

Results

Table 4.4(ii) continued

Term	$\text{LiN}_3$	$\text{NaN}_3(\alpha)$	$\text{NaN}_3(\beta)$	$\text{KN}_3$	$\text{RbN}_3$	Units
$\partial U_{\text{ad}}/\partial a$	-17.2	-10.2	-33.8	-20.3	-21.4	
$\partial U_{\text{ad}}/\partial b$	-28.1	-17.5	-	-	-	$\text{kJ.mol}^{-1}$
$\partial U_{\text{ad}}/\partial c$	-4.2	-6.3	-2.3	-11.2	-10.3	$\text{\AA}^{-1}$
$U_{\text{qd}}$	4.0	2.5	2.3	3.0	3.2	$\text{kJ.mol}^{-1}$
$\partial U_{\text{ad}}/\partial a$	-2.9	-1.3	-4.2	-2.3	-2.6	
$\partial U_{\text{ad}}/\partial b$	-4.5	-2.2	-	-	-	$\text{kJ.mol}^{-1}$
$\partial U_{\text{ad}}/\partial c$	-0.3	-0.7	-0.2	-1.4	-1.3	$\text{\AA}^{-1}$
$\bar{r}_{\text{M}}$	0.424	0.875	0.875	1.191	1.317	$\text{\AA}$
$U_{\text{R}}^{++}$	0.3	1.0	0.9	3.1	3.7	$\text{kJ.mol}^{-1}$

Results

Table 4.4(iii) Intermediate results for cesium,  
ammonium, thallium, silver and  
copper(I) azides.

Term	CSN <sub>3</sub>	NH <sub>4</sub> N <sub>3</sub>	TlN <sub>3</sub>	AgN <sub>3</sub>	CuN <sub>3</sub>	Units
A <sub>0</sub>	629.2	663.0	664.6	708.1	692.8	
U <sub>M</sub>	A <sub>1</sub>	2361.8	2381.9	2367.3	2289.0	2199.2 kJ.mol <sup>-1</sup>
	A <sub>2</sub>	4172.8	4216.2	4206.6	4156.0	4129.9
U <sub>SE</sub>	B <sub>1</sub>	-2368.3	-2375.2	-2385.0	-2354.4	-2369.2 kJ.mol <sup>-1</sup>
	B <sub>2</sub>	-4145.5	-4156.6	-4173.8	-4120.3	-4146.0
	C <sub>0</sub>	629.2	663.0	664.6	708.1	692.8
U <sub>ELEC</sub>	C <sub>1</sub>	-7.1	-6.9	-17.7	-65.5	-170.0 kJ.mol <sup>-1</sup>
	C <sub>2</sub>	27.3	35.9	32.9	35.8	-16.2
$\left(\frac{\partial U_{ELEC}}{\partial a}\right)_{a=a_0}$	D <sub>a0</sub>	-86.2	-38.2	-104.3	-84.0	-3.1
	D <sub>a1</sub>	-43.1	-19.5	-52.5	-61.4	95.3 kJ.mol <sup>-1</sup>
	D <sub>a2</sub>	-27.5	-11.7	-37.1	-29.6	14.8 Å <sup>-1</sup>
$\left(\frac{\partial U_{ELEC}}{\partial b}\right)_{b=b_0}$	D <sub>b0</sub>	-	-31.6	-	-65.8	-
	D <sub>b1</sub>	-	-10.0	-	-10.8	- kJ.mol <sup>-1</sup>
	D <sub>b2</sub>	-	-11.1	-	-32.0	- Å <sup>-1</sup>
$\left(\frac{\partial U_{ELEC}}{\partial c}\right)_{c=c_0}$	D <sub>c0</sub>	-7.5	-12.9	-1.9	25.5	-119.2
	D <sub>c1</sub>	30.7	60.7	41.3	78.8	-38.1 kJ.mol <sup>-1</sup>
	D <sub>c2</sub>	4.5	5.3	7.5	23.8	-11.4 Å <sup>-1</sup>
U <sub>dd</sub>		41.2	38.9	85.4	91.0	62.3 kJ.mol <sup>-1</sup>

continued over

Results

Table 4.4(iii) continued

Term	CsN <sub>3</sub>	NH <sub>4</sub> N <sub>3</sub>	TlN <sub>3</sub>	AlN <sub>3</sub>	CuN <sub>3</sub>	Units
$\Delta H_f^\circ$	-24.6	-8.4	-52.9	-30.4	-24.0	
$\Delta H_f^\circ$	-	-6.7	-	-24.9	-	kJ.mol <sup>-1</sup>
$\Delta H_f^\circ$	-10.7	-21.8	-25.0	-38.0	-29.7	g <sup>-1</sup>
$U_{qd}$	4.4	3.8	9.8	11.2	6.7	kJ.mol <sup>-1</sup>
$\Delta H_f^\circ$	-3.5	-1.1	-7.7	-4.8	-3.0	
$\Delta H_f^\circ$	-	-1.1	-	-3.6	-	kJ.mol <sup>-1</sup>
$\Delta H_f^\circ$	-1.5	-2.9	-4.0	-6.9	-4.0	g <sup>-1</sup>
$\bar{r}_M$	1.465	1.265	1.370	1.1*	1.0*	Å
$U_R^{++}$	4.1	2.6	6.0	8.1	3.0	kJ.mol <sup>-1</sup>

\* rough estimate only

Results

In all the metal azides considered here (including ammonium) the cation is taken as spherical and a basic radius is required. For the alkali metal, ammonium and thallium ions values are taken from Jenkins and Pratt (1977a). No values as yet exist for either the silver or copper(I) ions, in view of the results shown in Figure 2.8(vii) however it was felt an estimate was sufficient at this stage (the results obtained made the assignment of accurate radii unwarranted). The values used for the cation basic radii and the subsequent cation-cation contributions to the repulsion energy are given in Tables 4.4(ii) and 4.4(iii).

A repulsion model of the azide ion has to be developed. Considering the ion as composed of three spheres we can write a Huggins and Mayer type expression for the repulsion energy in a metal azide as:

$$\begin{aligned}
 U_R = & \frac{1}{2} b c_{NN} \exp\left(\frac{2F_N}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{NNi}}{\rho}\right) + b c_{NN'} \exp\left(\frac{F_N + F_{N'}}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{NN'i}}{\rho}\right) + \\
 & b c_{NN'} \exp\left(\frac{F_N + F_{N'}}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{NN'i}}{\rho}\right) + \frac{1}{2} b c_{N'N'} \exp\left(\frac{2F_{N'}}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{N'N'i}}{\rho}\right) + \\
 & b c_{NN'} \exp\left(\frac{2F_N}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{NN'i}}{\rho}\right) + b c_{N'N'} \exp\left(\frac{F_{N'} + F_N}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{N'N'i}}{\rho}\right) \quad 4.4(ii)
 \end{aligned}$$

where most of the symbols are defined in Equations 2.3(iii)-2.3(v). N' refers to the central nitrogen atom of

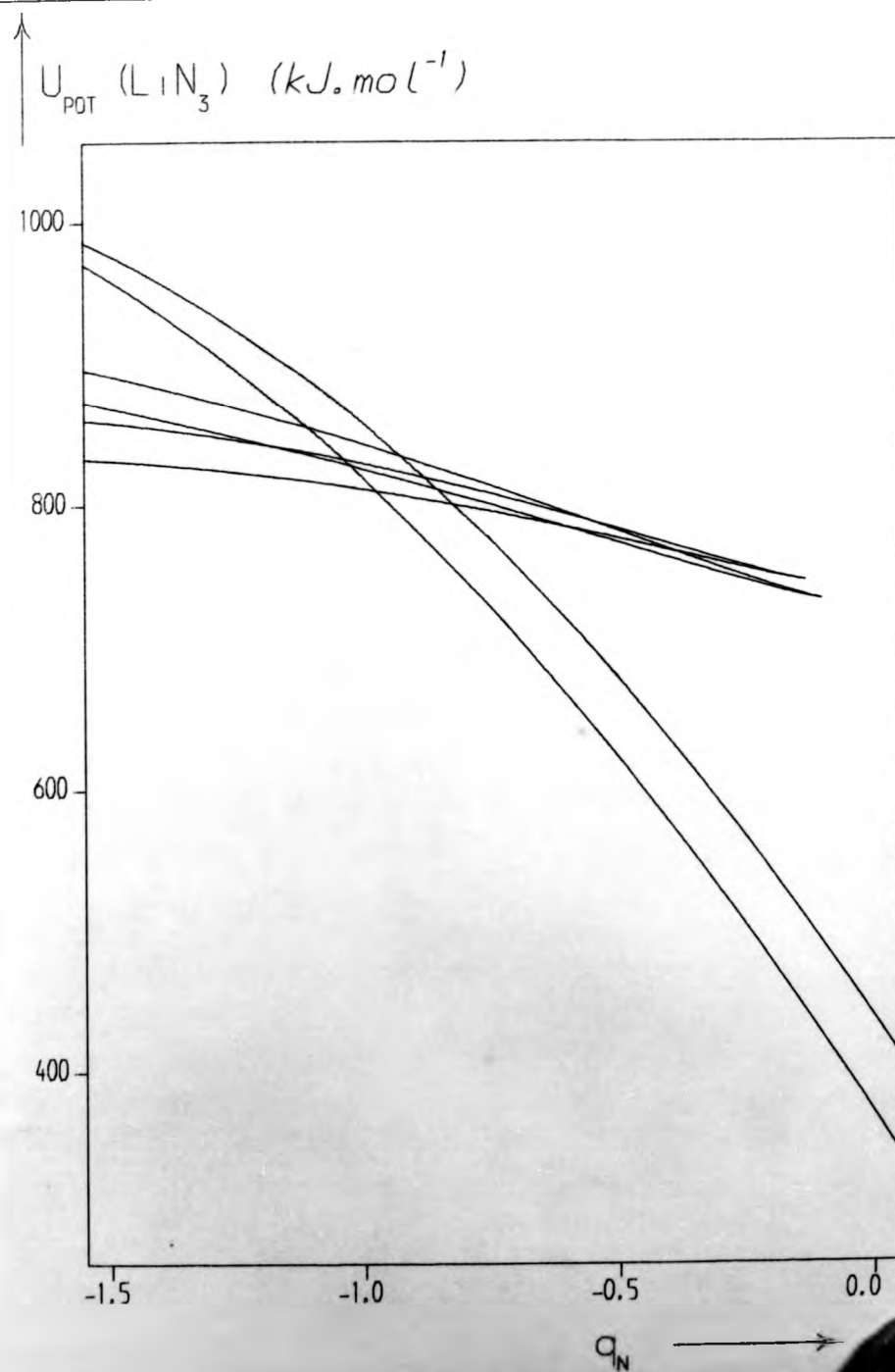
## Results

the azide ion and  $M$  to a terminal atom. The metal ion is assumed to have a known basic radius so there are two unknown radii in the above equation. The method can only deal with one unknown and so a further approximation must be made. One obvious possibility is to assume the radii are equal, i.e. a repulsion model of three equal spheres centered on the nitrogen atoms. This model will exaggerate the contribution from the central nitrogen as this will possess a smaller radius than the terminal atoms, owing to a smaller negative charge. The other possibility is to put  $r_M = 0$ . This is presumably the other side of the 'true' situation from the first model. Calculations are reported here using both models.

The curves of lattice energy against charge on the terminal nitrogens can now be plotted, for each independent cell direction and both models. After listing each plot the individual curves are codified in their order on the left-hand ordinate (from low to high lattice energy) in brackets.  $M_i^j$  refers to the  $M$  salt, the derivative in the  $i$  direction using model  $j$  (1 is the three sphere model and 2 is the two sphere model). The curves for lithium azide are shown in Figure 4.4(i) ( $Li_a^2$ ,  $Li_a^1$ ,  $Li_b^2$ ,  $Li_b^1$ ,  $Li_o^1$ ,  $Li_o^2$ ). The curves for the polymorphs of sodium azide (the monoclinic form,  $Na(M)$ , and the trigonal

#### Results

Figure 4.4(i) Lattice energy of lithium azide.



form,  $\text{Na(T)}$ ) are shown in Figure 4.4(ii) ( $\text{Na(M)}_a^2$ ,  $\text{Na(T)}_a^2$ ,  $\text{Na(H)}_a^1$ ,  $\text{Na(T)}_a^1$ ,  $\text{Na(K)}_b^2$ ,  $\text{Na(M)}_b^1$ ,  $\text{Na(T)}_c^2$ ,  $\text{Na(T)}_c^1$ ,  $\text{Na(M)}_c^1$ ,  $\text{Na(M)}_c^2$ ). Figure 4.4(iii) ( $\text{K}_c^2$ ,  $\text{K}_c^1$ ,  $\text{K}_a^2$ ,  $\text{K}_a^1$ ) shows the curves for potassium azide. The curves for rubidium, cesium and thallium azide are not shown as they are very similar, due to identical structure types, to those of potassium. Figure 4.4(iv) ( $\text{NH}_{4c}^2$ ,  $\text{NH}_{4c}^1$ ,  $\text{NH}_{4b}^2$ ,  $\text{NH}_{4b}^1$ ,  $\text{NH}_{4a}^2$ ,  $\text{NH}_{4a}^1$ ) shows curves for ammonium azide. Figure 4.4(v) ( $\text{Ag}_b^1$ ,  $\text{Ag}_b^2$ ,  $\text{Ag}_a^2$ ,  $\text{Ag}_c^2$ ,  $\text{Ag}_a^1$ ,  $\text{Ag}_c^1$ ) shows the curves for silver azide and Figure 4.4(vi) ( $\text{Cu}_a^1$ ,  $\text{Cu}_a^2$ ,  $\text{Cu}_c^2$ ,  $\text{Cu}_c^1$ ) for copper(I) azide.

The assignment of values from the above figures is made from the intersection points. However it is apparent that some intersections can be taken as more reliable than others, for instance in Figure 4.4(i) the intersection between the curves resulting from the a and b derivatives cannot be considered anywhere as near as reliable as between a and c and b and c due to the angles of intersection. There is then a definite case for only including certain intersection points in our assignments. Intersections between curves resulting from different models are also not considered, their inclusion could not be justified theoretically. The intersection points to be considered for the three sphere model are listed in Table 4.4(iv) and those for the two sphere model in Table

#### Results



Figure 4.4(ii) Lattice energy of the pleomorphs of sodium azide.

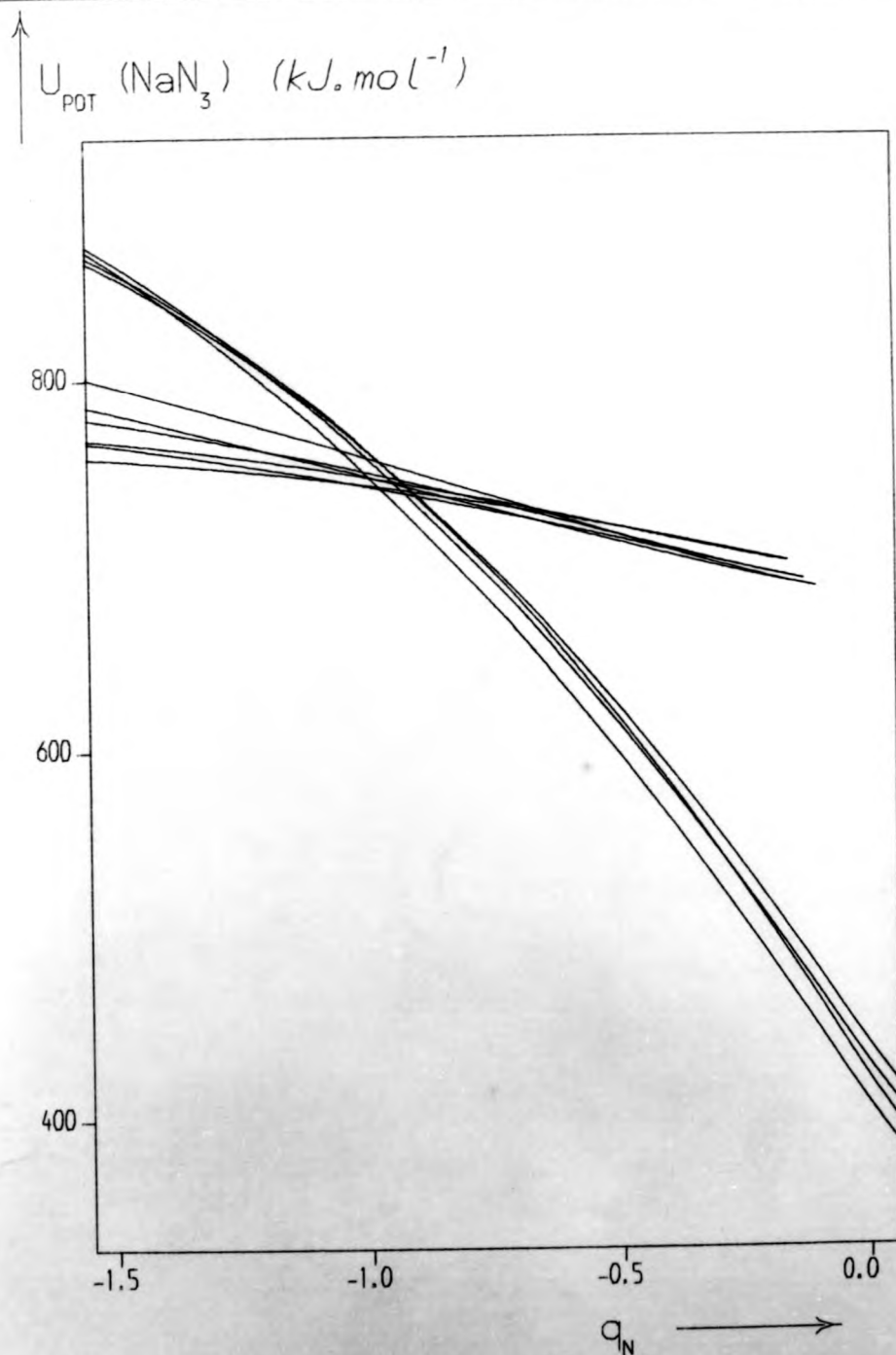


Figure 4.4(iii) Lattice energy of potassium azide.

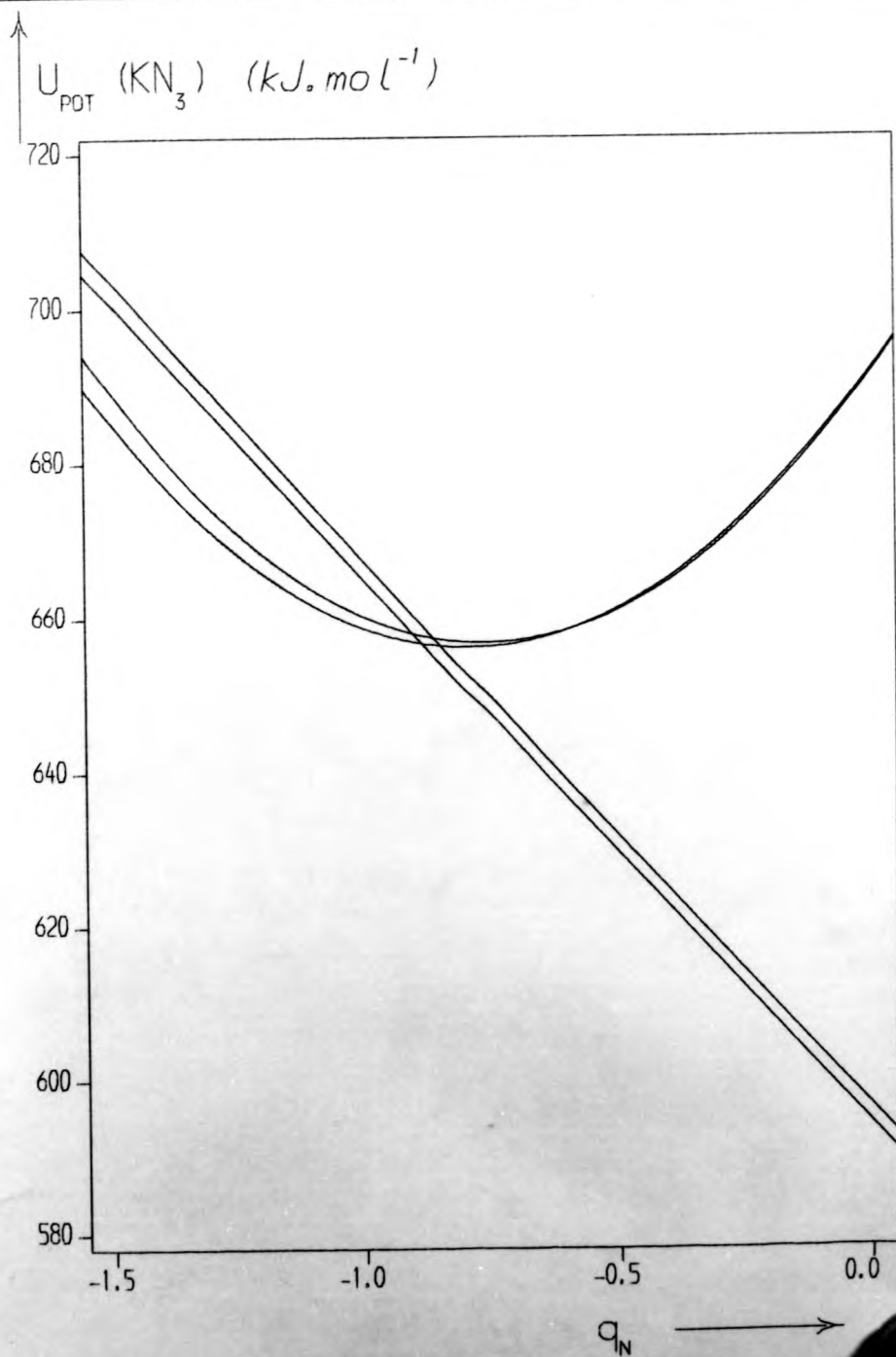


Figure 4.4(iv) Lattice energy of ammonium azide.

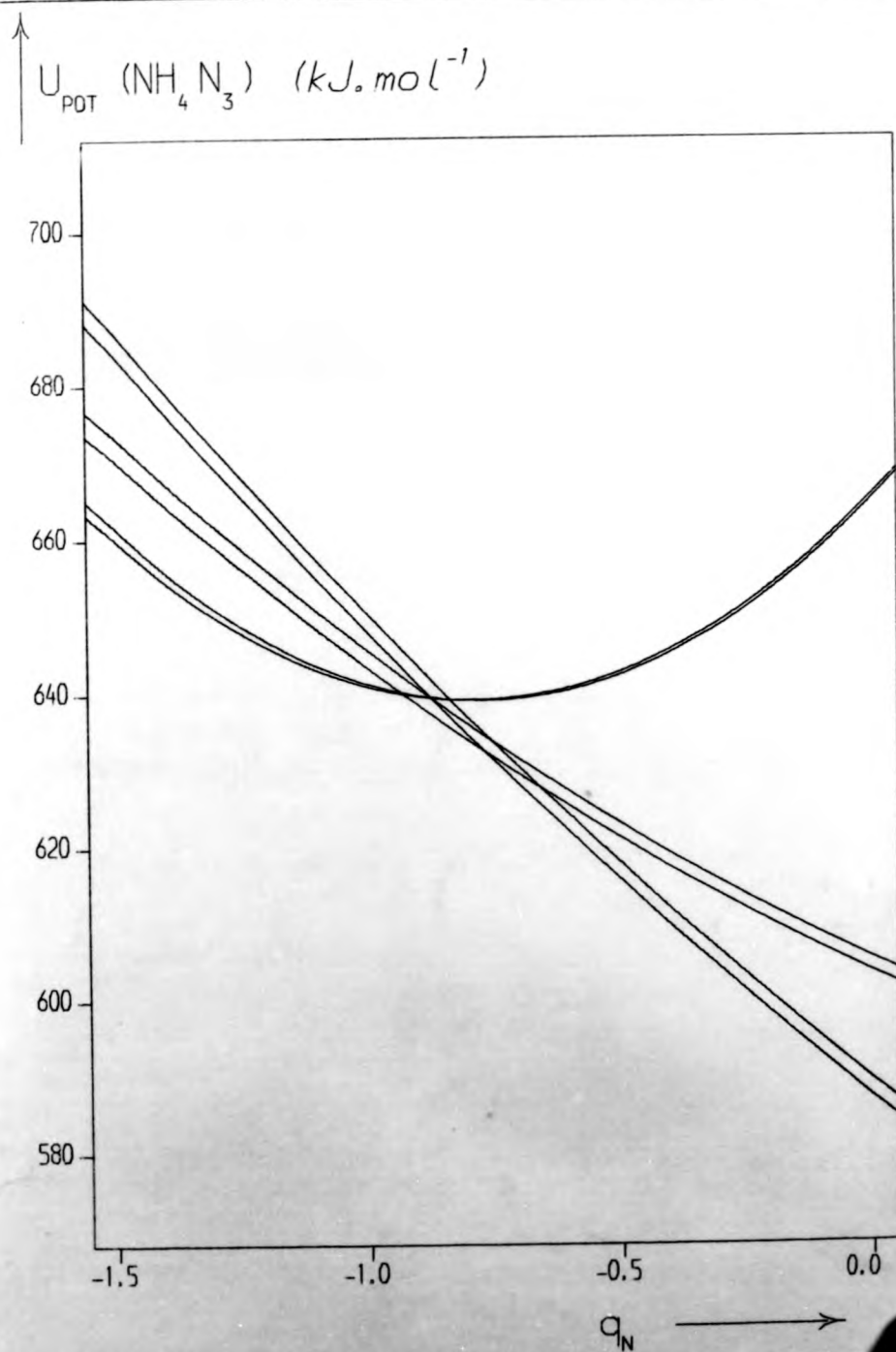


Figure 4.4(v) Lattice energy of silver azide.

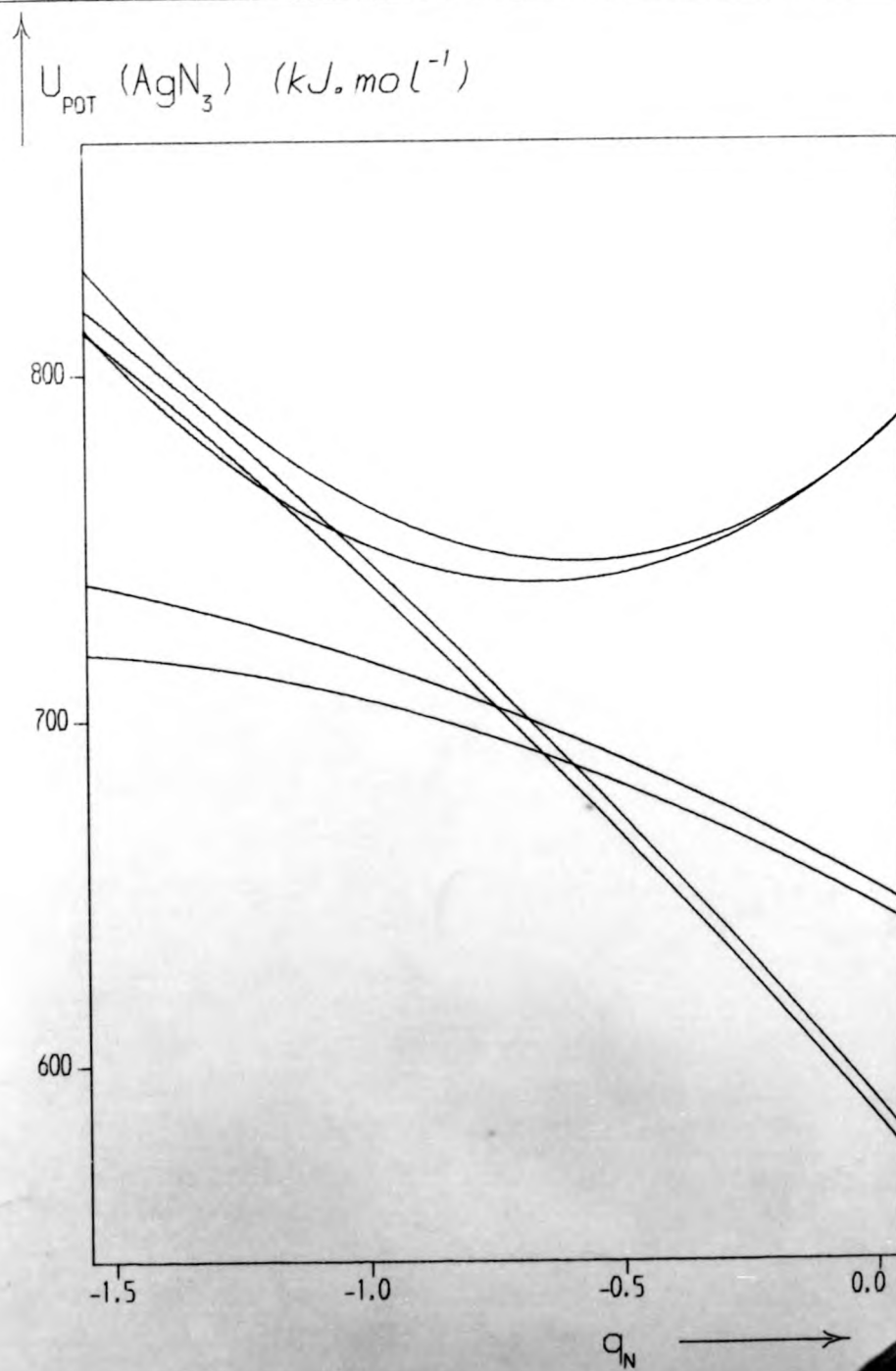


Figure 4.4(vi) Lattice energy of copper(I) azide.

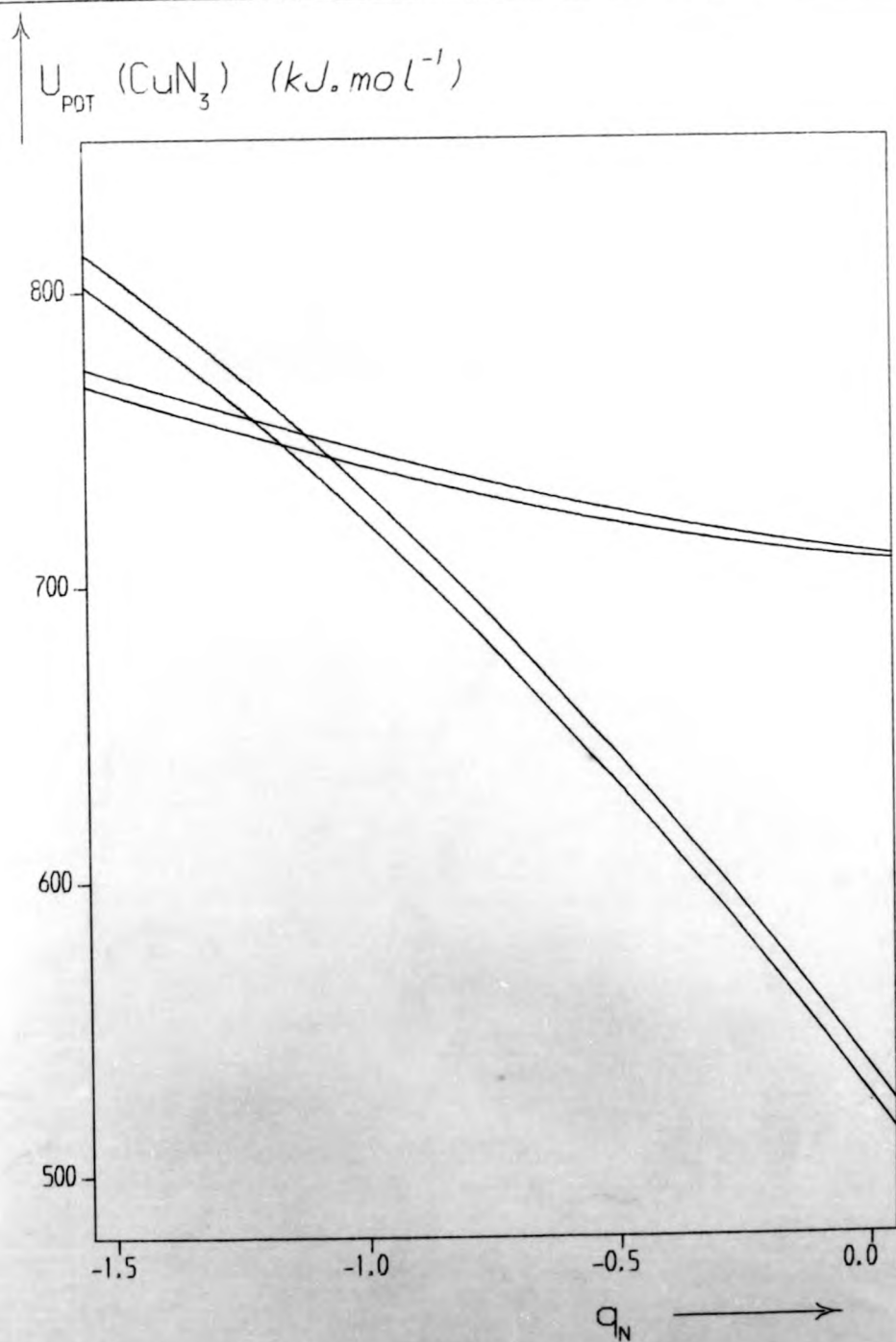


Table 4.4(iv) Coordinates of the intersection points on Figures 4.4(i)-4.4(vi) using the three sphere model of the azide ion.

Salt	Curves	$q_N$	$\bar{r}_N(\text{\AA})$	$U_{\text{POT}} (\text{kJ.mol}^{-1})$
$\text{LiN}_3$	ac	-1.039	1.171	832.1
	bc	-1.109	1.156	654.7
$\text{NaN}_3(\text{M})^*$	ac	-0.994	1.161	746.5
	bc	-1.051	1.149	761.4
$\text{NaN}_3(\text{T})^*$	ac	-0.935	1.150	745.3
$\text{KCN}_3$	ac	-0.860	1.073	657.4
$\text{FeN}_3$	ac	-0.815	1.075	633.0
$\text{CsN}_3$	ac	-0.703	1.087	606.2
$\text{NH}_4\text{N}_3$	ac	-0.836	1.103	639.2
	bc	-0.876	1.111	639.5
$\text{TiN}_3$	ac	-0.776	1.086	663.2
$\text{CuN}_3$	ac	-1.064	1.015	743.3

\* (M) indicates the monoclinic polymorph and  
(T) the trigonal

Results

4.4(v). The values for the basic radius of the nitrogen atoms obtained at these points are also listed.

Tables 4.4(iv) and 4.4(v) show some interesting points.

(a) Silver azide shows no intersections which could be used to assign values. The curve derived from the c derivative is above the other two (see Figure 4.4(v)). There seems to be no obvious reason for a breakdown in the isotropic assumption and so these results appear to bring the crystal structure data (or chemical composition) into some doubt. Even if a tentative value was assigned a similar situation to that for the copper(I) salt would arise in the thermochemistry (see later).

(b) There is some difference in the values obtained from the a and b derivatives (at intersection) of the monoclinic forms of lithium and sodium azide. This is probably due to some anisotropy caused by the greater polarising power of these small ions.

(c) The polarising power of the ions is also seen when noticing the general trend of decreasing charge distribution going down the series from lithium to cesium. The more polarising the ion the greater its effect of separating the charge in the anion. The effect is not however very large.

## Results



Table 4.4(v) Coordinates of the intersection points on Figures 4.4(i)-4.4(vi) using the two sphere model for the azide ion.

Salt	Curves	$q_N$	$\bar{r}_N (\text{\AA})$	$U_{\text{POT}} (\text{kJ} \cdot \text{mol}^{-1})$
$\text{LiN}_3$	ac	-0.823	1.253	800.4
	bc	-0.653	1.248	810.6
$\text{NaN}_3(\text{M})^*$	ac	-0.932	1.227	739.9
	bc	-0.944	1.224	743.2
$\text{NaN}_3(\text{T})^*$	ac	-0.899	1.225	736.5
$\text{KN}_3$	ac	-0.882	1.175	656.7
$\text{RLiN}_3$	ac	-0.873	1.173	634.0
$\text{CsN}_3$	ac	-0.778	1.176	607.4
$\text{NH}_4\text{N}_3$	ac	-0.873	1.201	639.4
	bc	-0.929	1.214	639.9
$\text{TLiN}_3$	ac	-0.849	1.183	664.5
$\text{CuN}_3$	ac	-1.217	1.110	756.4

\* (M) indicates the monoclinic pleomorph and (T) the trigonal



(d) The potassium, rubidium, cesium and thallium salts which all have similar structures (with space group  $I4/mcm$ ) give smaller values for the basic radii than the others (excluding the copper(I) salt). This is presumably a manifestation of some property of the structure.

In order to assign actual values a choice has to be made between the two repulsion models. Tables 4.4(iv) and 4.4(v) show that both are flexible enough to give similar (and presumably reasonably accurate) results, this is to be expected as the central nitrogen plays a much smaller role in the repulsion energy than the terminal atoms. The 'true' repulsion envelope is expected to lie somewhere between the two models, with the three sphere model intuitively nearer to it. However the results of the two sphere model appear more internally consistent (much closer intersection ranges) and so it is felt that a straight average of the results from the two models is the best approach that can be adopted.

The results for the lattice energies are given in Table 4.4(vi) along with the standard deviation (SD) obtained from the averaging. The results are based on the individually found charge distributions. The overall average (with standard deviation) for the charge

## Results

Table 4.4(vi) Lattice energies assigned for azide salts and enthalpy of formation of the gaseous azide ion ( $\text{kJ}\cdot\text{mol}^{-1}$ ).

Salt	$U_{\text{POT}} (\text{MN}_3)$			SD	$\Delta H_f^\circ (\text{N}_3^-)(\text{g})$
	3 sphere	2 sphere	Average		
$\text{LiN}_3$	843	805	824	24	148
$\text{NaN}_3(\alpha)$	754	742	748	9	159*
$\text{NaN}_3(\beta)$	745	737	741	6	152*
$\text{KN}_3$	657	657	657	1	142
$\text{RLN}_3$	633	634	633	1	138
$\text{CsN}_3$	606	607	607	1	145
$\text{NH}_4\text{N}_3$	639	640	640	0	121
$\text{TLN}_3$	663	665	664	1	120
$\text{CuN}_3$	743	756	750	9	-59

\* assuming the transition enthalpy is zero

## Results

distribution however is:

$$q_N = -0.90 \pm 0.10 \quad 4.4(\text{iii})$$

obtained from the values for the three sphere model  $(-0.92 \pm 0.13)$  and the two sphere model  $(-0.88 \pm 0.05)$ . The average basic radii (with standard deviation) obtained are (noting the earlier point about some structures tending to give smaller values), for the three sphere model:

$$\bar{r}_N = 1.12 \pm 0.04 \text{ \AA} \quad 4.4(\text{iv})$$

and for the two sphere model:

$$\bar{r}_N = 1.21 \pm 0.03 \text{ \AA} \quad 4.4(\text{v})$$

A thermochemical cycle can be used to combine the results obtained onto one figure. The cycle involving both the lattice energy and the enthalpy of formation of the gaseous azide ion produces the equation:

$$\Delta H_f^\circ(\text{N}_3^-)(g) = U_{\text{POT}}(\text{MN}_3) + \Delta H_f^\circ(\text{MN}_3)(o) - \Delta H_f^\circ(\text{M}^+)(g) + nRT \quad 4.4(\text{vi})$$

where  $n=0$  for monatomic M and  $n=3/2$  for ammonium. This

## Results

is applied to the individual lattice energies and the results are given in Table 4.4(vi). The thermochemical data is listed in Table 4.4(vii).

In Table 4.4(vi) the alkali metal salts show a certain degree of uniformity in the values for the enthalpy of formation of the gaseous azide ion, although they are perhaps not as constant as one might hope. The values for the other salts however show results very much at variance, one with another. The extremely large discrepancy found in the case of the copper(I) salt could not possibly be explained in terms of methodological errors arising in the calculation, it must, therefore, be a consequence of either an extremely inaccurate value for the enthalpy of formation of the crystalline salt or a totally inaccurate crystal structure. Both could be caused by large amounts of impurity, most likely different oxidation states of the elements. In fact Wyckoff (1965) lists the crystal structure of copper azide amongst nitride rather than azide salts. The results for this salt are not considered further here.

The lattice energy of ammonium azide leads to a result for the enthalpy of formation of the gaseous azide ion about  $20-30 \text{ kJ.mol}^{-1}$  lower than for other salts. This

#### Results

Table 4.4(vii) Thermochemical data for azide salts  
(kJ.mol<sup>-1</sup>).

Salt	$\Delta H_f^\circ(\text{N}_3)(\text{s})$ a	$\Delta H_f^\circ(\text{M}^+)(\text{g})$	Source
LiN <sub>3</sub>	17.9	687.2	b
NaN <sub>3</sub> *	21.3	609.8	b
KN <sub>3</sub>	-1.3	514.2	b
RbN <sub>3</sub>	-0.4	494.9	c
CsN <sub>3</sub>	-10.0	452.3	b
NH <sub>4</sub> N <sub>3</sub>	112.1	630.2	d
TlN <sub>3</sub>	233.6	777.7	e
AgN <sub>3</sub>	310.6	1019.2	f
CuN <sub>3</sub>	281.3	1090.0	f

\* enthalpy of transition between the two polymorphs is unknown, it is assumed negligible

a taken from Gora, Downs, Kemmey and Sharma (1977)

b Stull and Prophet (1971)

c Rossini et al (1952)

d Jenkins and Morris (1976)

e Wagman et al (1968)

f Wagman et al (1969)

## Results

energy gap can be explained by hydrogen bonding stabilising the structure. These latter results are not included in the final averaging.

A similar result is obtained from calculations on the thallium salt where hydrogen bonding is not a possibility. Comparing the current results with those of Jenkins and Pratt (1977c), where the results for thallium azide fit in with those for the alkali metal salts, we see that almost all the 'discrepancy' is due to a lower dispersion energy in this case, caused by the adoption of a different (lower) polarisability for the thallium ion. Because of this the calculations with the new method were repeated taking the polarisability used previously. These calculations gave an intersection (on the two sphere model) between the two curves at  $q_N = -0.69$ ,  $U_{POT}(TlN_3) = 674 \text{ kJ.mol}^{-1}$ . The lattice energy is higher, although not sufficiently so, but the charge distribution now seems inconsistent with our other results. Consequently this does not solve the problem. A major factor that could be involved here is the high polarisability of the ion causing anisotropy, this would mean unreliable intersection points. It is clear that thallium salts in general demand extra attention and they are a subject which needs a major investigation. The results (both) are

#### Results

omitted from the final averaging.

Figure 4.4(vii) shows a plot of enthalpy of formation of the gaseous azide ion versus the charge on the terminal nitrogen atom for all the salts considered except silver and copper(I) azide. From this figure we can assign (with a standard deviation):

$$\Delta H_f^\circ(\text{N}_3^-)(g) = 149 \pm 14 \text{ kJ.mol}^{-1} \quad 4.4(\text{vii})$$

This value, and the charge distribution and lattice energies quoted earlier, agree well with those of Jenkins and Pratt (1977c) showing that the Jenkins and Addington equation can be generally used for this type of salt. This agreement reinforces the argument given in that work concerning the much higher value for the thermochemical function quoted in the standard thermochemical tables.

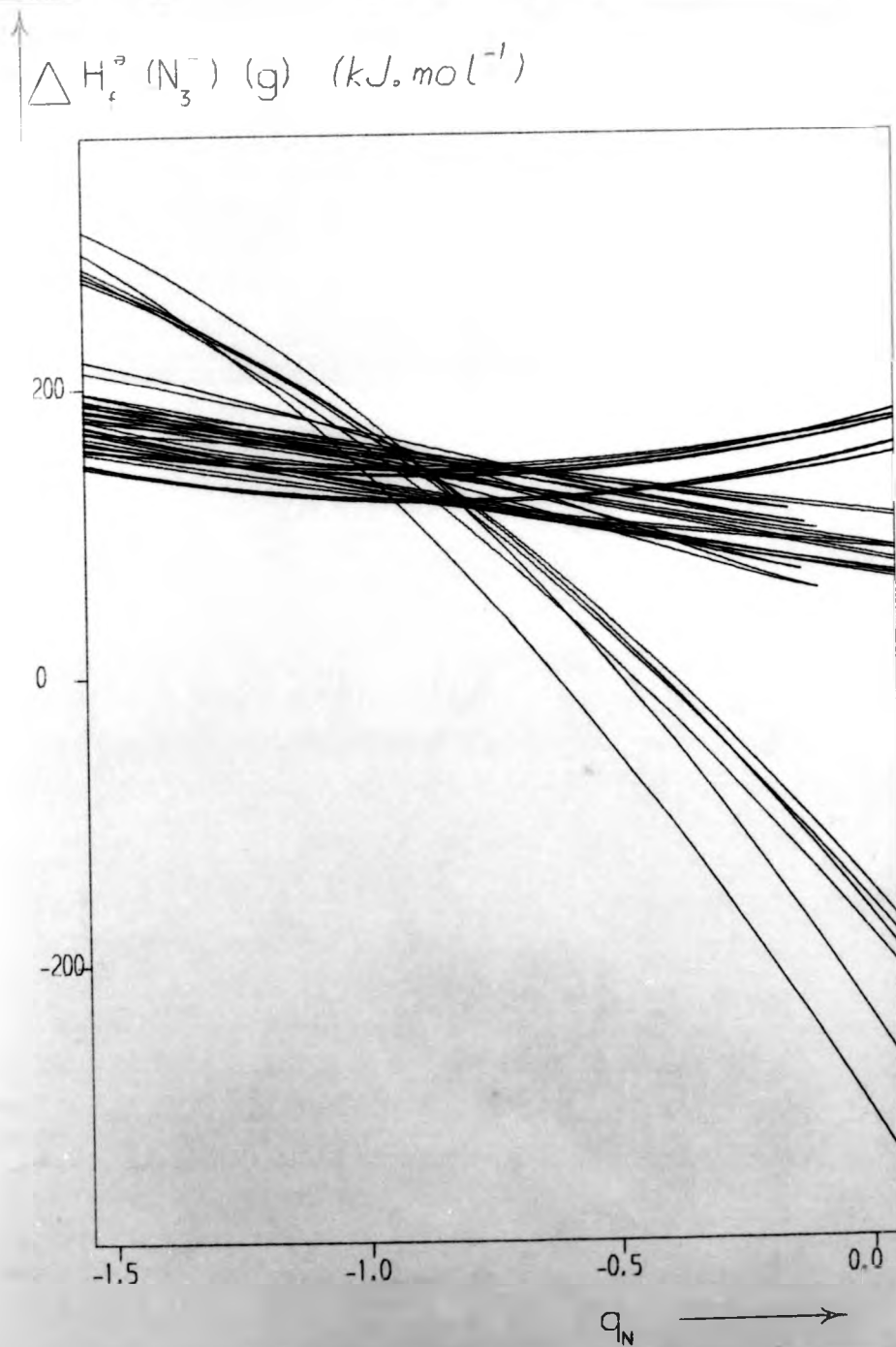
Using a relationship equivalent to Equation 4.3(xix) with the data  $\Delta H_f^\circ(\text{N}_3^-)(aq) = 275.1 \text{ kJ.mol}^{-1}$  (Wagman et al (1968)) enables us to assign the conventional and absolute hydration enthalpies of the gaseous azide ion as:

$$\Delta H_{\text{conv hyd}}^\circ(\text{N}_3^-)(g) = -1410 \text{ kJ.mol}^{-1} \quad 4.4(\text{viii})$$

$$\Delta H_{\text{abs hyd}}^\circ(\text{N}_3^-)(g) = -310 \text{ kJ.mol}^{-1} \quad 4.4(\text{ix})$$

## Results

Figure 4.4(vii) Enthalpy of formation of the gaseous azide ion.





The large amount of recently reviewed data concerning azide salts promised an excellent opportunity to produce data concerning the azide ion and to test the newly proposed method. In view of this it has to be said that some of the calculations, dealing with non-alkali metal salts, yielded rather unsatisfactory results which is naturally disappointing. It is suspected that this is purely due to unreliable data. However Figure 4.4(vii) does show that **most** of the calculations yielded apparently good reliable results so validating the new method.

#### 4.5 The Bifluoride Ion

In this research the Jenkins and Waddington equation has been applied to the alkali metal bifluoride salts and the results published in the paper by Jenkins and Pratt (1977d). The application of the new method to these salts has not yet been described, the results are presented here, with the inclusion of ammonium bifluoride.

The obvious similarities between the azide and bifluoride ions leads to salts that possess similar crystal structures along with other common factors. Like

#### Results

the azide ion the difluoride ion has previously been considered as capable of being approximated by a solid ellipsoid (Waddington (1958); Dixon, Jenkins and Waddington (1972); Jenkins and Waddington (1975b)) but unlike this ion there is another obvious approximation that could be made, one of two separated fluorine ions, also considered in the above studies. The validity of both of these models has been brought into doubt by the application of the Jenkins and Waddington equation. The work of Jenkins and Pratt (1977d) gives thermochemical results much more in line with those obtained by quantum mechanical studies. The possibility of applying the new method gives the opportunity of obtaining a further set of lattice energy results.

The discussion regarding the treatment of the azide ion as an ellipsoid (see Section 4.4) applies also to the difluoride ion. the exaggeration of the electron density around the central atom of the ion is however much more pronounced in this case. The treatment of the ion as two separated fluorine ions would seem a much more reasonable model, presenting an upper limit for the repulsion energy, with any non-classical distribution of charge leading to deviation from this ideal. The charge is assumed to be distributed between the hydrogen ( $q_H$ ) and fluorine ( $q_F$ )

## Results

atoms such that:

$$q_H + 2 q_F = -1 \quad 4.5(i)$$

The crystal structures used in this study are the same as those used in the published part of this research with the exception of that for ammonium bifluoride, this salt was not treated in that study. The details of the unit cells of these structures are given in Table 4.5(i).

The electrostatic energy and derivatives (using a parameterisation equivalent to the Equations 4.3(viii)-4.3(xi)) for the alkali metal salts are given in Table 4.5(ii). The hydrogen positions for the ammonium ions in ammonium fluoride have been experimentally obtained and so the electrostatic terms can be further parameterised in terms of the charge distribution inside the ammonium ion:

$$q_N + 4 q_H = 1 \quad 4.5(ii)$$

where  $q_N$  is the charge on the nitrogen and  $q_H$  the charge on the ammonium hydrogen atoms. Introducing a second subscript the notation becomes:

$$U_M = \sum_{i=0}^2 \sum_{j=0}^2 A_{ij} q_H^i q_F^j \quad \text{where } i + j \leq 2 \quad 4.5(iii)$$

## Results

Table 4.5(i) Unit cell details for bifluoride salts.

Salt	Space group	z	Cell constants ( $\text{\AA}$ )			H-F distance	Ref.
			a	b	c		
$\text{LiHF}_2$	$\text{P}\bar{3}_1$	3	3.003	(=a)	13.186	1.134	a
$\text{NaHF}_2$	$\text{P}\bar{3}_1$	3	3.476	(=a)	13.76	1.134	b
$\text{KHF}_2$	$\text{I}4/\text{mcm}$	4	5.67	(=a)	6.81	1.129	c
$\text{RbHF}_2$	$\text{I}4/\text{mcm}$	4	5.90	(=a)	7.25	1.129*	c
$\text{CsHF}_2$	$\text{I}4/\text{mcm}$	4	6.14	(=a)	7.84	1.129*	c
$\text{In}_4\text{HF}_2$	$\text{P}6_{3\text{mm}}$	4	8.408	8.163	3.670	1.138	c

\* assumed from the potassium salt, supported by the corresponding azide ion salts

Table 4.5(ii) Intermediate results for alkali metal  
bifluorides.

Term	LiHF <sub>2</sub>	NaHF <sub>2</sub>	KHF <sub>2</sub>	RbHF <sub>2</sub>	CsHF <sub>2</sub>	Units
$A_0$	707.7	708.2	727.3	697.9	667.6	
$U_M$	$A_1$	1923.2	2146.9	2450.0	2455.6	2463.7 kJ.mol <sup>-1</sup>
	$A_2$	4110.8	4197.6	4354.3	4346.9	4341.3
$U_{SE}$	$B_1$	-2450.3	-2450.6	-2461.1	-2461.3	-2461.5 kJ.mol <sup>-1</sup>
	$B_2$	-4288.0	-4288.6	-4306.9	-4307.2	-4307.6
	$C_0$	707.7	708.2	727.3	697.9	667.6
$U_{ELBC}$	$C_1$	-527.1	-303.6	-11.1	-5.7	2.2 kJ.mol <sup>-1</sup>
	$C_2$	-177.1	-91.1	47.4	39.7	33.6
$(\frac{\partial U_{ELBC}}{\partial a})_{a=a_0}$	$D_{a0}$	150.2	45.8	-122.5	-107.9	-92.2
	$D_{a1}$	702.3	396.7	-74.5	-62.7	-53.3 kJ.mol <sup>-1</sup>
	$D_{a2}$	266.1	127.7	-56.5	-44.2	-34.4 g <sup>-1</sup>
$(\frac{\partial U_{ELBC}}{\partial c})_{c=c_0}$	$D_{c0}$	-87.9	-63.0	-4.8	-8.4	-13.0
	$D_{c1}$	-56.4	-43.5	52.1	42.3	33.1 kJ.mol <sup>-1</sup>
	$D_{c2}$	-4.8	-4.1	10.0	7.1	4.6 g <sup>-1</sup>
$U_{ad}$		22.4	28.3	37.9	39.1	46.1 kJ.mol <sup>-1</sup>
$\frac{\partial U_{ad}}{\partial a}$		-31.5	-35.4	-29.5	-28.6	-31.3 kJ.mol <sup>-1</sup>
$\frac{\partial U_{ad}}{\partial c}$		-5.1	-5.8	-11.8	-11.8	-13.3 g <sup>-1</sup>

continued over

Results

Table 4.5(ii) continued

Term	LiHF <sub>2</sub>	NaHF <sub>2</sub>	KHF <sub>2</sub>	RbHF <sub>2</sub>	CsHF <sub>2</sub>	Units
$U_{qd}$	1.4	2.2	3.2	3.7	5.6	$\text{kJ.mol}^{-1}$
$\partial U_{qd}/\partial a$	-2.6	-3.8	-3.4	-3.6	-5.0	$\text{kJ.mol}^{-1}$
$\partial U_{qd}/\partial c$	-0.5	-0.6	-1.4	-1.6	-2.3	$\text{\AA}^{-1}$
$\bar{r}_M$	0.424	0.875	1.191	1.317	1.465	$\text{\AA}$
$U_R^{++}$	0.7	1.5	5.3	6.0	6.9	$\text{kJ.mol}^{-1}$

Results

similar equations hold for the other terms. The results for the electrostatic coefficients of ammonium bifluoride are given in Table 4.5(iii). The lack of a value for the charge distribution in the ammonium ion has meant resorting to a point charge of +1 at the nitrogen as is used in other cases where the hydrogen positions are not resolved. This should not introduce any large errors as the charge distribution should be small.

The literature contains no polarisability data for the bifluoride ion and so a dispersion model of two separated fluorine ions is adopted. The polarisabilities of Pirene and Kartheiser (1964) being employed. The results for the dispersion energy and cell length derivatives are given in Tables 4.5(ii) and 4.5(iii), along with the values for the cation basic radii employed (taken from earlier work) and the results for the cation-cation repulsion energy.

The only viable repulsion model for the anion is one of two spheres centered on the fluorine atoms, as the electron density surrounding the hydrogen atom in the ion must be minimal. The form of the Huggins and Mayer repulsion energy may be simply obtained from Equation

#### Results

Table 4.5(iii) Intermediate results for ammonium  
bifluoride ( $\text{kJ.mol}^{-1}$  and  $\text{kJ.mol}^{-1}.\text{g}^{-1}$ )

Term	i j	0 0	0 1	0 2	1 0	1 1	2 0
$L_M$		702.3	2447.0	4324.4	-6325.1	-61.1	19535.5
$U_{SE}^*$		0.0	-2442.5	-4274.4	6339.2	0.0	-19532.7
$U_{ELFC}$		702.3	1.9	44.2	14.1	-61.1	2.8
$(\partial U_{ELFC} / \partial a)_{a=a_0}$		-40.9	-24.3	-15.3	-2.9	14.7	1.3
$(\partial U_{ELFC} / \partial b)_{b=b_0}$		-34.4	-15.0	-14.5	-4.8	17.4	-0.7
$(\partial U_{ELFC} / \partial c)_{c=c_0}$		-21.1	76.7	6.7	-1.8	28.4	-5.9

$\gamma =$	$T$	$\frac{dT}{da}$	$\frac{dT}{db}$	$\frac{dT}{dc}$
$Q_{dd}$	42.5	-10.9	-11.3	-25.5
$U_{qd}$	4.4	-1.5	-1.6	-3.7

$$\bar{r}_M = 1.265 \text{ \AA} \quad U_R^{++} = 4.2 \text{ kJ.mol}^{-1}$$

\* a combination of the self energies of the two  
complex ions

## Results



4.4(ii). Adopting this model we can now plot the lattice energy versus the charge distribution in the anion for each derivative of each salt. The curves for the lithium salt are shown in Figure 4.5(i) (the curve resulting from the *a* derivative being below that from the *c* derivative at the left-hand ordinate). The curves for the sodium salt are similar. The plot for potassium bifluoride is shown in Figure 4.5(ii) (*a* above *c* at left), the curves for the rubidium and cesium salts being similar. The curves for ammonium bifluoride, with the ammonium ion considered as a point charge, are shown in Figure 4.5(iii) (at left, from the bottom to top, *c-b-a*).

Results for the lattice energies, charge distribution in the anion and the basic radius of the repulsion spheres considered can be obtained from the intersections on these figures, the coordinates of which are given in Table 4.5(iv). Some points concerning this table and the assignment of values are given below.

(a) The general decrease in the distribution of charge in the ion (for each structure) is again shown from lithium to cesium.

(b) The basic radii shown by the tetragonal salts are lower than those for the others, this is as was found in the azide salts and must be a property of this structure.

## Results

Figure 4.5(i) Lattice energy of lithium bifluoride.

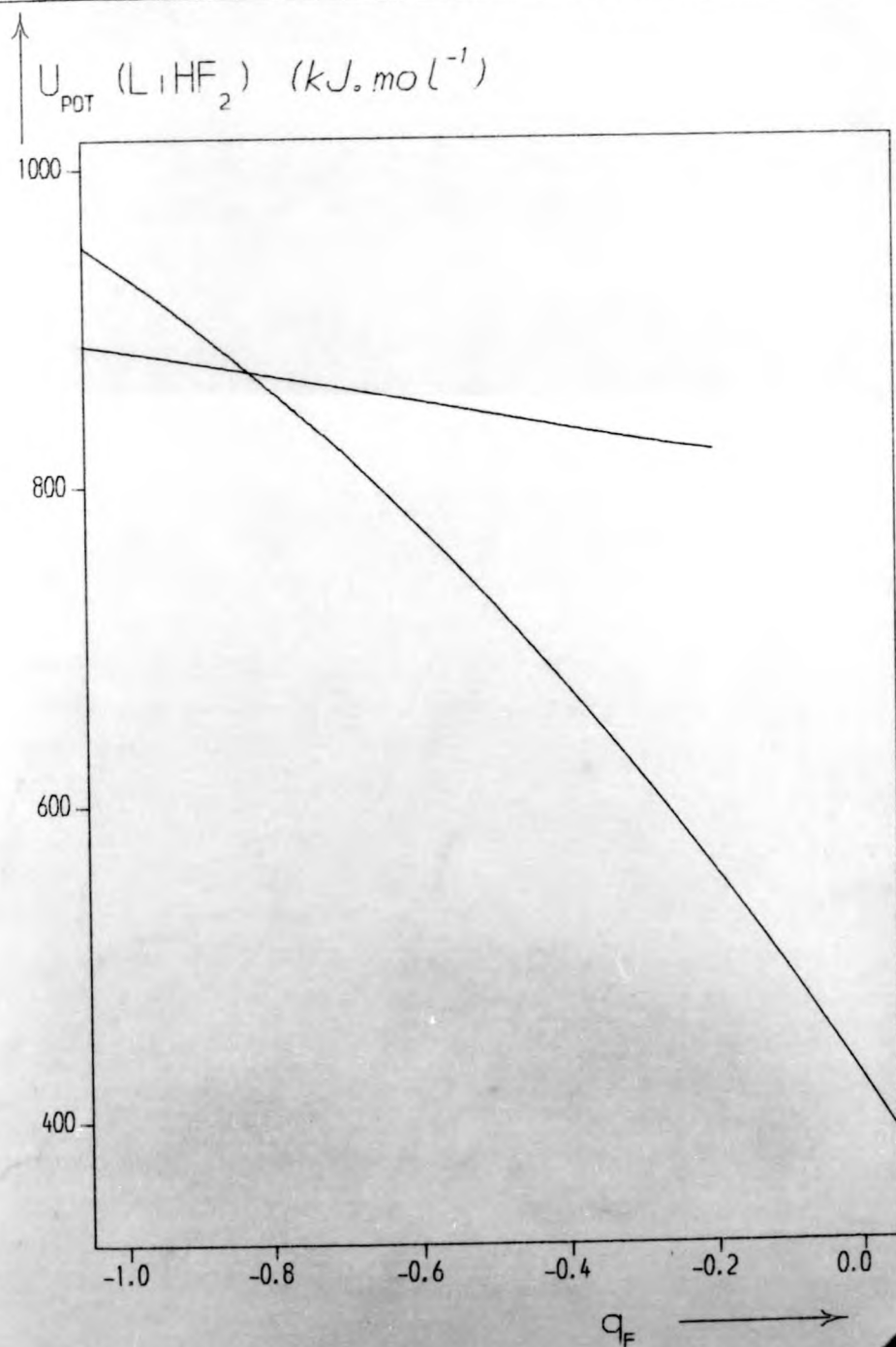


Figure 4.5(ii) Lattice energy of potassium bifluoride.

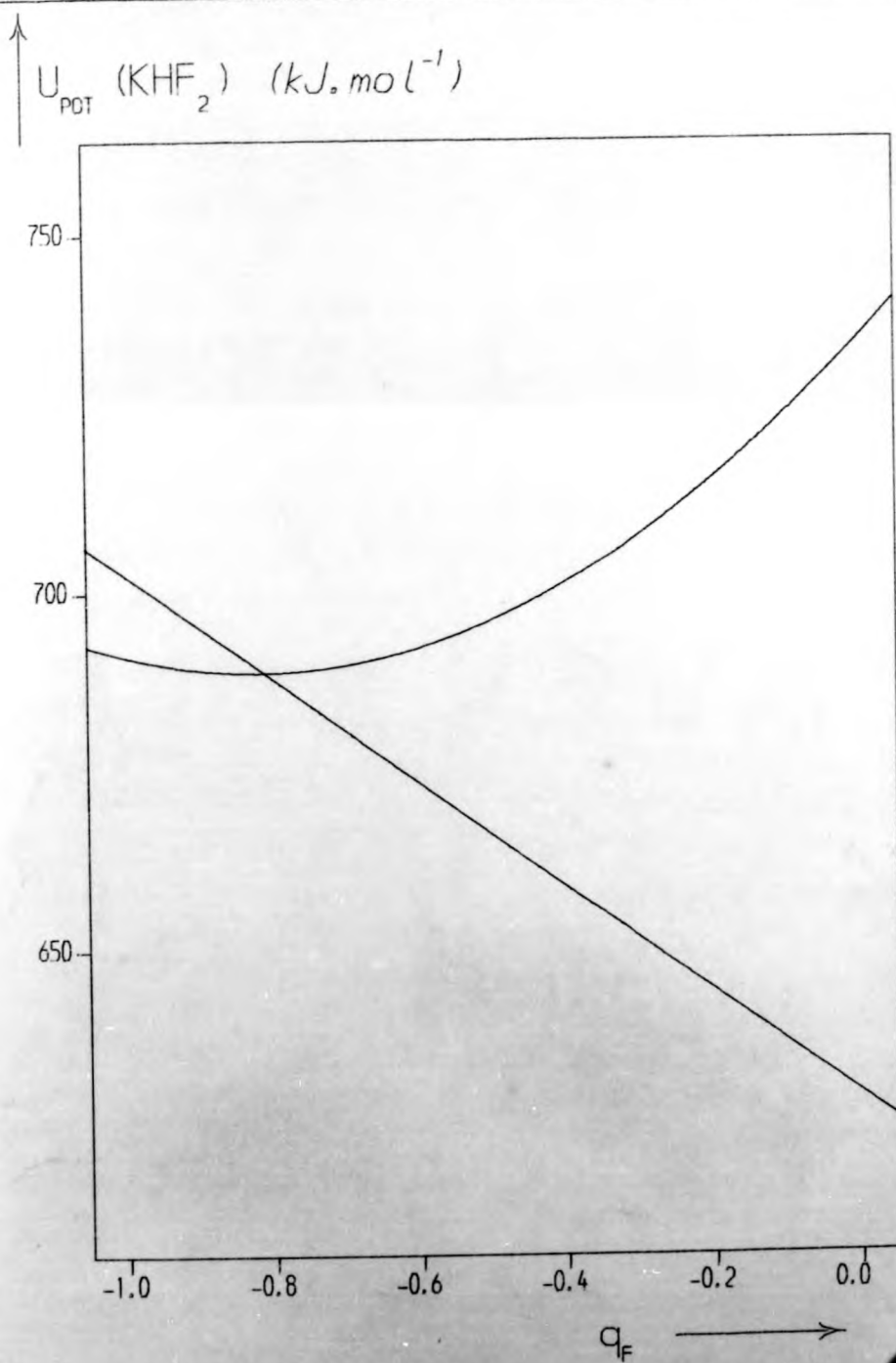
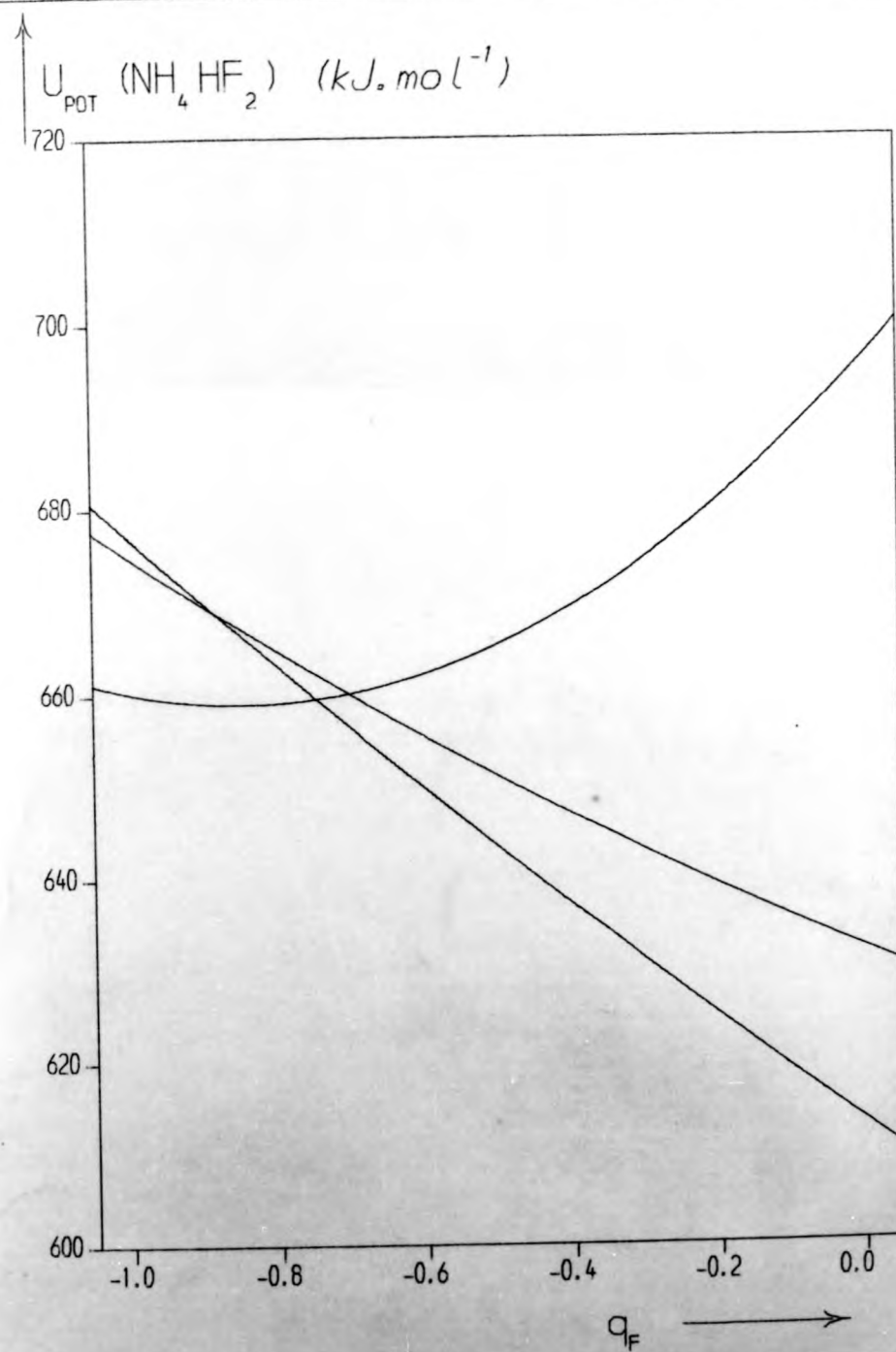


Figure 4.5(iii) Lattice energy of ammonium bifluoride.



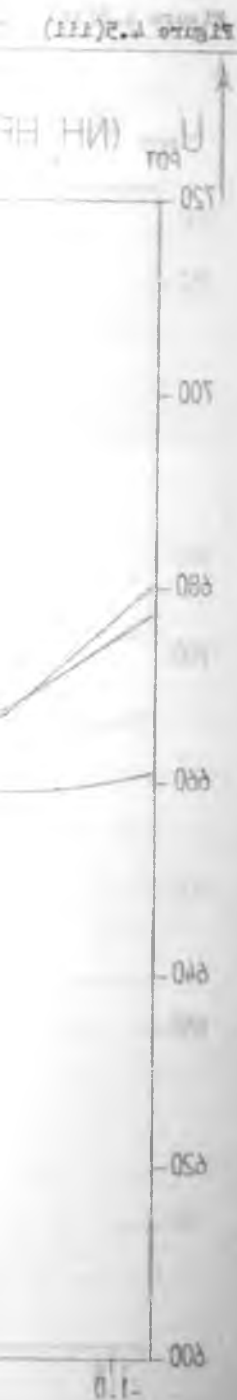


Table 4.5(iv) Coordinates of intersection points for  
bifluoride salts.

Salt	Intersection	$q_F$	$\bar{r}_F(\text{\AA})$	$U_{POT}(\text{kJ.mol}^{-1})$
LiHF <sub>2</sub>	ac	-0.823	1.090	872.5
NaHF <sub>2</sub>	ac	-0.766	1.071	770.8
KHF <sub>2</sub>	ac	-0.811	1.031	683.9
RbHF <sub>2</sub>	ac	-0.763	1.031	659.8
CsHF <sub>2</sub>	ac	-0.623	1.034	630.4
NH <sub>4</sub> HF <sub>2</sub>	at	-0.883	1.088	668.9
	ac	-0.746	1.081	659.6
	nc	-0.701	1.069	660.1

Results

(c) The lattice energies assigned for the alkali metal salts are as given in the table.

(d) For assignment of values from the results for ammonium bifluoride only the 'ac' and 'bc' intersections are considered due to the similar nature of the a and b curves. Accordingly:

$$U_{\text{POT}}(\text{NH}_4\text{HF}_2) = 660 \text{ kJ.mol}^{-1} \quad 4.5(\text{iv})$$

(e) The average charge distribution, with standard deviation, bearing in mind point (a), is:

$$q_{\text{F}} = -0.75 \pm 0.07 \quad 4.5(\text{v})$$

(f) The average basic radius of the fluorine atoms in the anion, noting point (b), is:

$$\bar{r}_{\text{F}} = 1.06 \pm 0.03 \text{ \AA} \quad 4.5(\text{vi})$$

A thermochemical cycle relating the lattice energy of a bifluoride salt to the enthalpy of formation of the gaseous bifluoride ion produces an equation:

$$\Delta H_{\text{F}}^{\circ}(\text{HF}_2^{-})(\text{g}) = U_{\text{POT}}^{\text{MHF}_2} + \Delta H_{\text{F}}^{\circ}(\text{MHF}_2)(\text{o}) - \Delta H_{\text{F}}^{\circ}(\text{M}^{+})(\text{g}) + nRT \quad 4.5(\text{vii})$$

completely analogous to that for the azide ion, where  $r=0$

## Results

for monatomic M and  $n=3/2$  for ammonium. Using this equation we can generate the plots in Figure 4.5(iv), from the lattice energy results and the thermodynamic data given in Table 4.5(v). The order of the curves, from bottom to top, at the left-hand ordinate is (where M symbolises the M salt and the derivative with respect to the i cell length):  $\text{NH}_{4\text{c}}$ ,  $\text{NH}_{4\text{b}}$ ,  $\text{NH}_{4\text{a}}$ ,  $\text{Rb}_\text{c}$ ,  $\text{K}_\text{c}$ ,  $\text{Na}_\text{a}$ ,  $\text{Cs}_\text{c}$ ,  $\text{K}_\text{a}$ ,  $\text{Fr}_\text{a}$ ,  $\text{Li}_\text{a}$ ,  $\text{Cs}_\text{a}$ ,  $\text{Na}_\text{c}$ ,  $\text{Li}_\text{c}$ . The results from the ammonium salt are again at variance with those of the alkali metals, this could possibly be explained by hydrogen bonding, significant charge distribution in the ammonium ion or an error in thermochemical values. This latter reason could also explain a slight discrepancy in the results for the cesium salt. It is felt that an average of the results from the lithium, sodium, potassium and rubidium salts is a more accurate method of assignment, this leads to:

$$\Delta H_f^\circ(\text{HF}_2^-)(\text{g}) = -743 \pm 3 \text{ kJ.mol}^{-1} \quad 4.5(\text{viii})$$

where the quoted error is just the standard deviation of the average.

A thermochemical cycle which can be used to explore whether or not the enthalpies of formation of the gaseous

## Results

Figure 4.5(iv) Enthalpy of formation of the gaseous bifluoride ion.

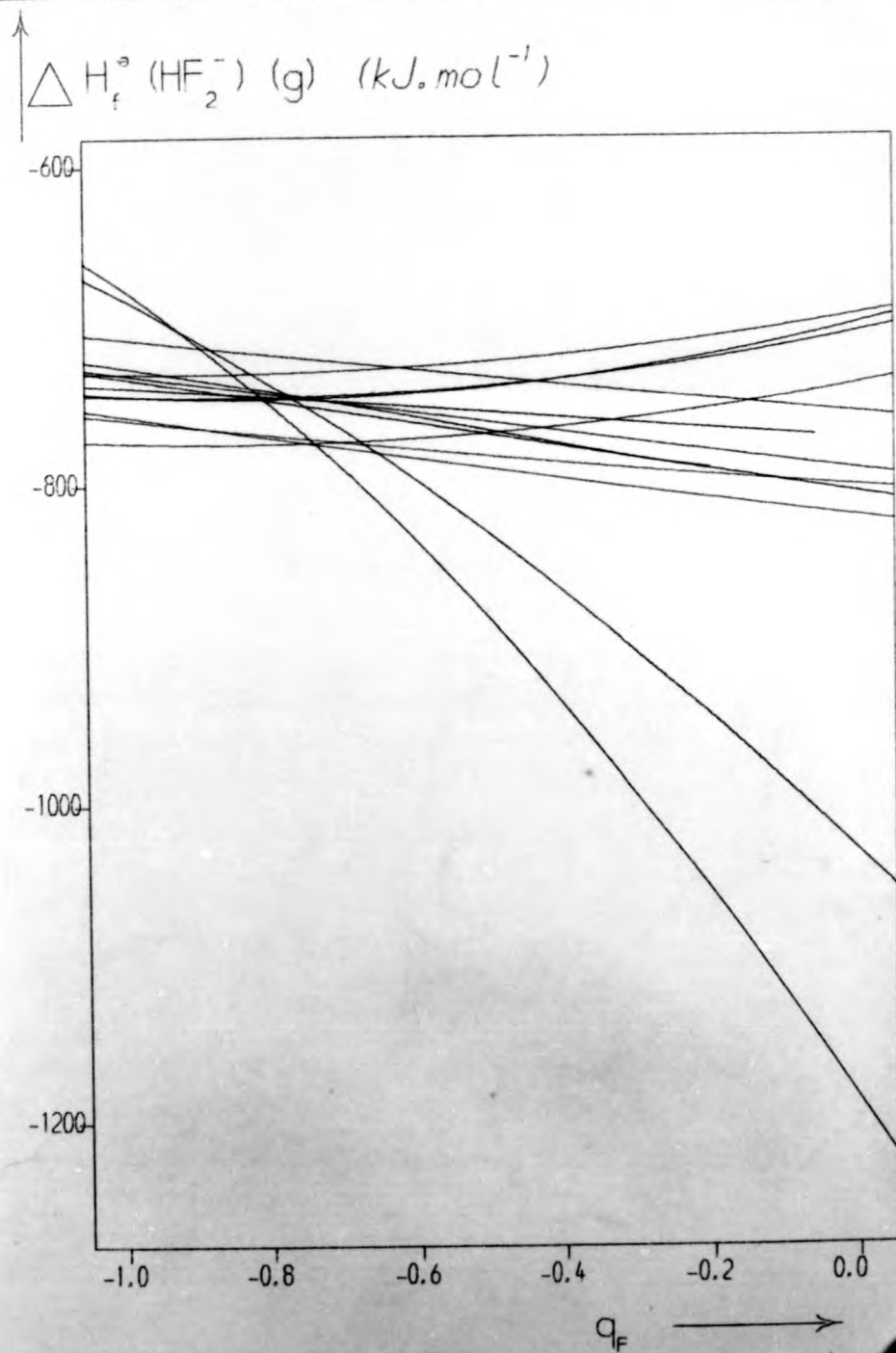




Table 4.5(v) Thermochemical data for difluoride and fluoride salts ( $\text{kJ. mol}^{-1}$ ).

M	$\Delta_{\text{H}}^{\circ}(\text{MF}_2)(\text{c})$	$\Delta_{\text{H}}^{\circ}(\text{MF})(\text{c})$	$\Delta_{\text{H}}^{\circ}(\text{M}^+)(\text{g})$	$U_{\text{POT}}(\text{MF})$
Li	-323.9a	-611.7c	687.2d	1030f
Na	-306.3a	-569.0c	629.8d	905f
K	-323.4a	-562.8c	514.2d	800f
Rb	-302.2a	-551.5c	494.9a	765f
Cs	-304.2a	-545.2c	452.3d	734f
Th	-382.9b	-464.0b	630.2e	753g

a Rossini et al(1952)

b Wajman et al(1968)

c Morris(1968)

d Stull and Prophet(1971)

e Jenkins and Morris(1976)

f Jenkins and Pratt(1977a)

g Section 4.2

Results

ammonium or cesium ions are at fault is shown in Figure 4.5(v). The cycle is independent of the enthalpy of formation of the gaseous cations. The quantity  $\Delta H_1^\circ$  (the negative of the fluoride ion affinity of gaseous hydrogen fluoride) is a measure of the hydrogen bond strength in the bifluoride ion. The equality produced from this cycle is:

$$\Delta H_1^\circ = U_{\text{POT}}(\text{MF}) - U_{\text{POT}}(\text{MHF}_2) + (m-n)RT - \Delta H_f^\circ(\text{MHF}_2)(\text{c}) + \Delta H_f^\circ(\text{MF})(\text{c}) + \Delta H_f^\circ(\text{HF})(\text{g}) \quad 4.5(\text{ix})$$

where  $m=-1$  for monatomic M and  $m=1/2$  for ammonium.

The enthalpies of formation of the fluoride salts are given in table 4.5(v) and  $\Delta H_f^\circ(\text{HF})(\text{g}) = -271.1 \text{ kJ.mol}^{-1}$  (Wagman et al(1968)). The lattice energies for the alkali metal fluorides are taken from Jenkins and Pratt (1977a). The lattice energy of ammonium fluoride is taken from the work described in Section 4.2 which was carried out in order to evaluate the basic radius of the ammonium ion. A plot of  $\Delta H_1^\circ$  versus  $r_f$  for the six salts is given in Figure 4.5(vi) (the order at the lefthand ordinate is  $\text{Li}_0$ ,  $\text{Na}_0$ ,  $\text{NH}_{4a}$ ,  $\text{NH}_{4b}$ ,  $\text{NH}_{4c}$ ,  $\text{Cs}_a$ ,  $\text{Rb}_a$ ,  $\text{K}_a$ ,  $\text{Li}_a$ ,  $\text{Rb}_0$ ,  $\text{Na}_a$ ,  $\text{K}_0$ ,  $\text{Cs}_0$ ). The discrepancy found earlier for the cesium salt

#### Results

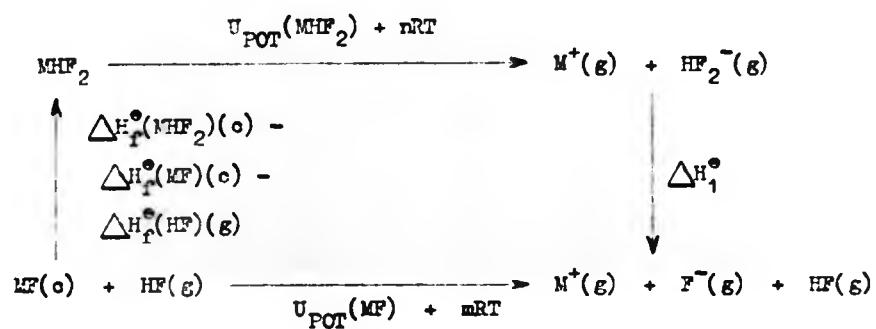
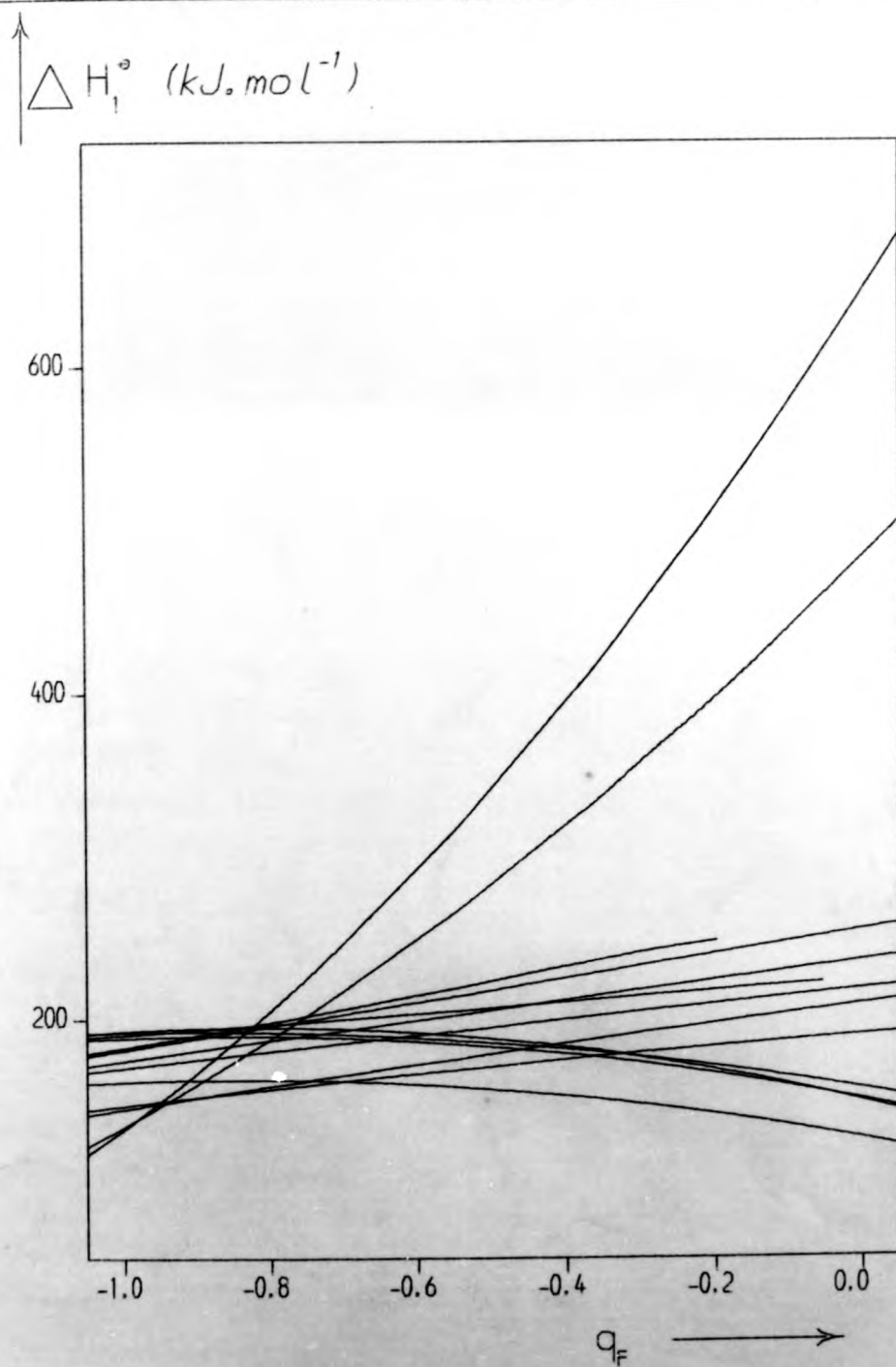


Figure 4.5(v) Thermochemical cycle giving the hydrogen bond strength of the bifluoride ion.

Figure 4.5(v) Hydrogen bond strength of the bifluoride ion.



seems to be absent here indicating a possible error of the order of  $10 \text{ kJ.mol}^{-1}$  in the enthalpy of formation of the gaseous cesium ion used there, assuming all the other data is consistent. Despite some reduction in the discrepancy found for the results from the ammonium salt there is still a considerable difference between these and those from the alkali metal salts. The reduction could indicate an error in the enthalpy of formation of the gaseous ion, whilst the continued difference probably indicates substantial interionic hydrogen bonding in both ammonium fluoride and bifluoride. From Figure 4.5(vi), neglecting the results from the ammonium salt, we can assign:

$$\Delta H_1^\circ = 194 \pm 4 \text{ kJ.mol}^{-1} \quad 4.5(x)$$

Using the experimental data  $\Delta H_f^\circ(\text{HF}_2^-)(\text{aq}) = -649.9 \text{ kJ.mol}^{-1}$  (Wagman et al(1968)), the relationship:

$$\Delta H_{\text{hyd}}^\circ(\text{HF}_2^-)(\text{g}) = \Delta H_f^\circ(\text{HF}_2^-)(\text{aq}) - \Delta H_f^\circ(\text{H}^+)(\text{g}) - \Delta H_f^\circ(\text{HF}_2)(\text{g}) - \Delta H_{\text{hyd}}^\circ(\text{H}^+)(\text{g}) \quad 4.5(xi)$$

and the data under Equation 4.7(xix) leads to:

$$\Delta H_{\text{conv hyd}}^\circ(\text{HF}_2^-)(\text{g}) = -1443 \text{ kJ.mol}^{-1} \quad 4.5(xii)$$

$$\Delta H_{\text{abs hyd}}^\circ(\text{HF}_2^-)(\text{g}) = -343 \text{ kJ.mol}^{-1} \quad 4.5(xiii)$$

#### Results

Similar to the values obtained for the azide ion, as would be expected.

Jenkins and Pratt (1977d) have reviewed other literature values of the results presented here. The lattice energies and thermochemical results obtained are about 10-20 kJ.mol<sup>-1</sup> different to those reported in that work, mainly attributable to the smaller charge distribution found in this study. The hydrogen bond strength is still in line with quantum mechanical estimates.

The difference between the results obtained from the new method and the Jenkins and Maddington equation indicate the possible source of inaccuracy introduced by the use of simple equations to calculate lattice energies. Although it should be noted that this equation seems to produce better results than earlier work which did not utilise the concept of energy minimisation.

#### 4.6 Hexahalometallate(IV) Ions

On the inception of the method described in Section 2.7 the major problem that prevented its immediate

#### Results

application to complex salts was the numerical evaluation of the cell length derivatives of Madelung constants (i.e. of electrostatic energies). The implementation as regards simple non-complex cubic salts (such as the alkali halides, Jenkins and Pratt (1977a)) was possible immediately, but only for the few cases where multiple moment expansions existed (or could be calculated at that time) could the necessary derivatives for other salts be obtained. Potassium hexachloroplatinate was an obvious case, just prior to the development of the new method Jenkins, Herzig and Neckel (1976) had calculated its multipole moment expansion with a view to calculating just the same derivative, in order to apply the Jenkins and Haddington equation to this salt (Jenkins (1977)). This multipole moment expansion was of the form:

$$U_{\text{ELEC}} = \frac{K}{a} \left\{ A_0 + \left( \sum_{\substack{i=2 \\ \text{even}}}^{32} A_i \left( \frac{d}{a} \right)^i q_{\mu} \right) + \left( \sum_{\substack{i=2 \\ \text{even}}}^{32} B_i \left( \frac{d}{a} \right)^i q_{\mu}^2 \right) \right\} \quad 4.6(i)$$

where  $a$  is the cubic cell side,  $d$  the platinum to chlorine distance in the hexachloroplatinate ion,  $A_i$  and  $B_i$  are the coefficients of the expansion and  $q_{\text{Cl}}$  is the charge on the chlorine atoms, assuming a charge distribution in the ion where:

$$q_{\text{Pt}} + 6 q_{\text{Cl}} = -2 \quad 4.6(ii)$$

#### Results

and  $q_{Pt}$  is the charge on the platinum atom. The coefficients are listed in Table 4.6(i), all odd coefficients are zero and a few early even terms cancel as well, due to symmetry. The summations in Equation 4.6(i) are strictly infinite series, but the number of terms is sufficient to give convergence to five decimal places in the Madelung constant. The existence of the expansion meant the new method could be applied to this salt, using the derivative expansion:

$$\left(\frac{\partial U_{elec}}{\partial a}\right)_d = \frac{-K}{a^2} \left\{ A_0 + \left( \sum_{\substack{i=2 \\ \text{even}}}^{32} (i+1) A_i \left(\frac{d}{a}\right)^i q_{Pt} \right) + \left( \sum_{\substack{i=2 \\ \text{even}}}^{32} (i+1) B_i \left(\frac{d}{a}\right)^i q_{Pt}^2 \right) \right\} \quad 4.6(iii)$$

The coefficients of the multipole expansion are not only independent of the unit cell side,  $a$ , but also the internal distance of the anion,  $d$ . These two parameters are sufficient to completely define the crystal structure of any hexahalometallate(IV) salt which crystallises with the  $K_2PtCl_6$  structure (space group  $Fm\bar{3}m$ ). This implies that Equations 4.6(i) and 4.6(iii) can be applied to any such salt and so these salts could also be treated by the new method. The first obvious use of this property was in the extension to other salts of the hexachloroplatinate ion, specifically the rubidium, cesium, ammonium and

## Results



Table 4.6(i) Coefficients for the multipole moment expansion of the Madelung constant of the potassium hexachloroplatinate structure.

$l$	$A_l$	$B_l$
0	11.636575	-
2	-	-
4	$1.1022116 \times 10^3$	-
6	$-4.0622573 \times 10^3$	-
8	$-1.2509071 \times 10^4$	$-6.3196620 \times 10^4$
10	$1.2784918 \times 10^5$	$4.6096205 \times 10^3$
12	$-9.8245131 \times 10^4$	$8.4924923 \times 10^5$
14	$-2.7800546 \times 10^6$	$1.4009900 \times 10^7$
16	$1.1697955 \times 10^7$	$-1.8021148 \times 10^8$
18	$3.0606899 \times 10^7$	$1.6707326 \times 10^7$
20	$-4.0185567 \times 10^8$	$3.7819129 \times 10^9$
22	$5.7592139 \times 10^8$	$4.7066195 \times 10^{10}$
24	$8.4920437 \times 10^9$	$-6.0126325 \times 10^{11}$
26	$-4.4153870 \times 10^{10}$	$1.1322937 \times 10^{11}$
28	$-7.2473810 \times 10^{10}$	$1.3300745 \times 10^{13}$
30	$1.4199835 \times 10^{12}$	$1.6548357 \times 10^{14}$
32	$2.9632121 \times 10^{12}$	$-2.1352191 \times 10^{15}$

Results

thallium salts, the results being given in Jenkins and Pratt (1977a) as an example of the application of this method. However there are very many other salts of general formula  $A_2MX_6$  of this symmetry which have had their crystal structures determined, involving transition metal and main group M with X as halogen. These have been treated in a systematic way in this research and the results presented in Jenkins and Pratt (1978c). It was found during this work that the lattice energy for salts where only the unit cell side, and not the atomic coordinates, had been experimentally obtained could be estimated from the other results (see later).

The development of the method to differentiate analytically the Bertaut method of electrostatic energy calculation, and the subsequent computer program (Jenkins and Pratt (1978a)) meant the general availability of the cell length derivatives of the electrostatic energy. For the cubic salts discussed above the results were confirmed, and now non-cubic salts could be considered. These salts include the added case where M is a lanthanide or actinide element, but are mainly salts where X is fluorine and the metals are as before. The results for the non-cubic salts are collected in Jenkins and Pratt (1978d).

#### Results

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#### Results

The criterion for selection of salts for consideration are:

- (a) their crystal structure is completely resolved (although for cubic salts with  $X=Cl$  estimates can be made using merely a unit cell length);
- (b) the atom M is in the  $+4$  oxidation state;
- (c) the hexahalometallate ion is a pure, or near pure, octahedron (i.e. near its free gaseous configuration).

This last point is guaranteed for the cubic salts but non-cubic structures had to be closely studied before beginning calculations. The details of the crystal structures extracted from the literature are given in Table 4.6(ii), in all cases, except where otherwise stated, the b unit cell length is equal to the a. This table, and all others in this section, are ordered primarily by the metal atom (transition metal (vertical groups), main group, lanthanide, actinide) and further by the halogen (fluorine to iodine) and cation (alkali metal followed by all others). There are 118 salts in this table, five with two polymorphic structures, giving 123 different structures for calculation.

The electrostatic energy and its cell length derivatives for the fully resolved cubic structures can be

## Results

Table 4.6(ii) Unit cell details for hexahalometalate(IV) salts.

Salt	Space group	Z	Cell constants (Å)			M-X Distance	Ref.
			a	b	c		
$\text{Na}_2\text{TiF}_6$	$\text{P}\bar{3}\text{m1}$	3	9.20	5.13	1.989	1	
$\text{K}_2\text{TiF}_6$	$\text{P}\bar{3}\text{m1}$	1	5.715	4.656	1.917	2	
$\text{K}_2\text{TiCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	9.792	-	2.350	1	
$\text{Rb}_2\text{TiCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	9.922	-	2.332	1	
$\text{Cs}_2\text{TiCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.219	-	2.350	1	
$(\text{NH}_4)_2\text{TiCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	9.89	-	2.374	1	
$\text{Rb}_2\text{TiBr}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.39	-	2.598	3	
$\text{Cs}_2\text{TiBr}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.57	-	2.643	3	
$\text{Li}_2\text{ZrF}_6$	$\text{P}\bar{3}1\text{n}$	1	4.973	4.656	2.016	4	
$\text{K}_2\text{ZrF}_6$	$\text{P}\bar{3}\text{m1}$	1	6.16	4.82	2.040	1	
$\text{Cs}_2\text{ZrF}_6$	$\text{P}\bar{3}\text{m1}$	1	6.41	5.01	2.035	1	
$\text{K}_2\text{ZrCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.08	-	-	5	
$\text{Rb}_2\text{ZrCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.178	-	2.443	1	
$\text{Cs}_2\text{ZrCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.407	-	2.446	1	
$\text{Rb}_2\text{HfF}_6$	$\text{P}\bar{3}\text{m1}$	1	6.134	4.815	2.033	6	
$\text{Cs}_2\text{HfF}_6$	$\text{P}\bar{3}\text{m1}$	1	6.39	5.00	2.029	6	
$\text{K}_2\text{HfCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.06	-	-	7	
$\text{K}_2\text{HfOCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	9.97	-	-	8	
$\text{Rb}_2\text{NbCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.10	-	-	8	
$\text{Cs}_2\text{NbCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	10.31	-	-	8	
$\text{K}_2\text{TaCl}_6$	$\text{Fm}\bar{3}\text{n}$	4	9.96	-	-	8	

continued over

Results

Table 4.6(ii) continued

Salt	Space group	Cell constants (Å)			M-X distance	Ref.
		z	a	c		
Pb <sub>2</sub> TaCl <sub>6</sub>	Fm 3n	4	10.11	-	-	9
Cs <sub>2</sub> TaCl <sub>6</sub>	Fm 3n	4	10.32	-	-	9
Cs <sub>2</sub> CrF <sub>6</sub>	Fm 3n	4	9.02	-	1.732	1
Li <sub>2</sub> MoF <sub>6</sub>	P4 22	2	4.686	9.191	1.939	9
K <sub>2</sub> MoCl <sub>6</sub>	Fm 3n	4	9.85	-	2.305	1
Pb <sub>2</sub> MoCl <sub>6</sub>	Fm 3n	4	9.99	-	-	1
Cs <sub>2</sub> MoCl <sub>6</sub>	Fm 3n	4	10.27	-	-	1
K <sub>2</sub> MoCl <sub>6</sub>	Fm 3n	4	9.875	-	2.360	10
Rb <sub>2</sub> MoCl <sub>6</sub>	Fm 3n	4	10.0	-	2.360	10
Cs <sub>2</sub> MoCl <sub>6</sub>	Fm 3n	4	10.27	-	2.362	10
Rb <sub>2</sub> MoF <sub>6</sub>	Fm 3n	4	10.50	-	2.478	10
Cs <sub>2</sub> MoF <sub>6</sub>	Fm 3n	4	10.70	-	2.482	10
K <sub>2</sub> MnF <sub>6</sub>	Ps 3n	2	5.67	9.35	1.755	1
Rb <sub>2</sub> MnF <sub>6</sub> (I)	P6 3n	2	5.855	9.503	1.720	1
Rb <sub>2</sub> MnF <sub>6</sub> (II)	Fm 3n	4	8.43	-	1.686	1
Cs <sub>2</sub> MnF <sub>6</sub>	Fm 3n	4	8.92	-	1.739	1
K <sub>2</sub> MnCl <sub>6</sub>	Fm 3n	4	9.645	-	2.276	11
Pb <sub>2</sub> MnCl <sub>6</sub>	Fm 3n	4	9.838	-	2.282	12
Cs <sub>2</sub> MnCl <sub>6</sub>	Fm 3n	4	10.17	-	-	11
(NH <sub>4</sub> ) <sub>2</sub> MnCl <sub>6</sub>	Fm 3n	4	9.82	-	2.239	12
Ni <sub>2</sub> TcCl <sub>6</sub>	Fm 3n	4	9.83	-	2.350	13
Rb <sub>2</sub> TcCl <sub>6</sub>	Fm 3n	4	9.965	-	-	14

continued over

Results

Table 4.4(ii) continued

Salt	Space group	z	Cell constants (Å)			M-X distance	Ref.
			a	b	c		
$K_2ReF_6$	$P\bar{3}m1$	1	5.879	4.611	1.953	15	
$K_2ReCl_6$	$Fm\bar{3}n$	4	9.84	-	2.153	16	
$Re_2ReCl_6$	$Fm\bar{3}n$	4	9.974	-	-	17	
$Cs_2ReCl_6$	$Fm\bar{3}n$	4	10.26	-	-	17	
$(NH_4)_2ReCl_6$	$Fm\bar{3}n$	4	9.98	-	-	18	
$K_2ReBr_6$	$Fm\bar{3}n$	4	10.385	-	2.483	16	
$K_2RuCl_6$	$Fm\bar{3}n$	4	9.739	-	-	1	
$K_2OsCl_6$	$Fm\bar{3}n$	4	9.729	-	2.364	1	
$Cs_2OsCl_6$	$Fm\bar{3}n$	4	10.230	-	-	19	
$(NH_4)_2OsCl_6$	$Fm\bar{3}n$	4	9.881	-	-	20	
$K_2OsBr_6$	$Fm\bar{3}n$	4	10.30	-	2.513	1	
$Ru_2CoF_6$	$Fm\bar{3}n$	4	8.45	-	1.700	21	
$Cs_2CoF_6$	$Fm\bar{3}n$	4	8.914	-	1.700	21	
$K_2RhF_6$	$P\bar{3}m1$	1	5.73	4.54	1.972	22	
$Ru_2RhF_6$	$P\bar{3}m1$	1	5.90	4.80	1.963	22	
$(NH_4)_2IrCl_6$	$Fm\bar{3}n$	4	9.87	-	2.469	1	
$K_2NiF_6$	$Fm\bar{3}n$	4	8.109	-	1.776	1	
$Ru_2NiF_6$	$Fm\bar{3}n$	4	8.462	-	1.709	1	
$K_2PdCl_6$	$Fm\bar{3}n$	4	9.74	-	-	1	
$Re_2PdCl_6$	$Fm\bar{3}n$	4	9.87	-	-	1	
$Cs_2PdCl_6$	$Fm\bar{3}n$	4	10.18	-	-	1	
$(NH_4)_2PdCl_6$	$Fm\bar{3}n$	4	9.84	-	2.300	23	

continued over

Results

Table 4.6(ii) continued

Salt	Space group	z	Cell constants (Å)		d-x distance	Ref.
			a	c		
$K_2PtF_6$	$P\bar{3}m1$	1	5.76	4.64	1.893	1
$K_2PtCl_6$	$Fm\bar{3}n$	4	9.755	-	2.341	1
$Ru_2PtCl_6$	$Fm\bar{3}n$	4	9.901	-	2.327	1
$Os_2PtCl_6$	$Fm\bar{3}n$	4	10.215	-	2.349	1
$(NH_4)_2PtCl_6$	$Fm\bar{3}n$	4	9.859	-	2.366	1
$Tl_2PtCl_6$	$Fm\bar{3}n$	4	9.799	-	2.303	1
$K_2PtBr_6$	$Fm\bar{3}n$	4	10.293	-	2.461	23
$Na_2SiF_6$	$P\bar{3}21$	3	8.859	5.038	1.683	24
$K_2SiF_6$	$Fm\bar{3}n$	4	8.133	-	1.749	1
$Ru_2SiF_6$	$Fm\bar{3}n$	4	8.452	-	1.690	1
$Os_2SiF_6$	$Fm\bar{3}n$	4	8.919	-	1.695	1
$(NH_4)_2SiF_6(I)$	$P\bar{3}m1$	1	5.76	4.77	1.659	1
$(NH_4)_2SiF_6(II)$	$Fm\bar{3}n$	4	8.395	-	1.688	25
$Tl_2SiF_6$	$Fm\bar{3}n$	4	8.568	-	1.714	1
$K_2GeF_6(HT)$	$P\bar{3}m1$	1	5.62	4.65	1.767	1
$K_2GeF_6(HI)$	$P6_3mc$	2	5.71	9.27	1.792	1
$Ru_2GeF_6(HT)$	$P\bar{3}m1$	1	5.82	4.79	1.774	1
$Ru_2GeF_6(HI)$	$P6_3mc$	2	5.94	9.63	1.863	1
$Os_2GeF_6$	$Fm\bar{3}n$	4	9.021	-	1.804	1
$(NH_4)_2GeF_6(I)$	$P\bar{3}m1$	1	5.85	4.775	1.773	1
$(NH_4)_2GeF_6(II)$	$Fm\bar{3}n$	4	8.46	-	1.717	1

continued over

Results



Table 4.e(ii) continued

Salt	Space group	z	Cell constants (Å)			M-X distance	Ref.
			a	b	c		
$\text{Cs}_2\text{GeCl}_6$	Fm3n	4	10.21	-	-	2.348	1
$\text{K}_2\text{SnCl}_6$	Fm3n	4	9.982	-	-	2.411	26
$\text{Rb}_2\text{SnCl}_6$	Fm3n	4	10.096	-	-	2.422	26
$\text{Cs}_2\text{SnCl}_6$	Fm3n	4	10.355	-	-	2.423	26
$(\text{NH}_4)_2\text{SnCl}_6$	Fm3n	4	10.044	-	-	2.422	26
$\text{Rb}_2\text{SnCl}_6$	Fm3n	4	9.97	-	-	2.393	1
$\text{Rb}_2\text{SnBr}_6$	Fm3n	4	10.64	-	-	2.607	1
$\text{Cs}_2\text{SnBr}_6$	Fm3n	4	10.81	-	-	2.648	1
$(\text{NH}_4)_2\text{SnBr}_6$	Fm3n	4	10.59	-	-	2.595	1
$\text{Rb}_2\text{SnI}_6$	Fm3n	4	11.60	-	-	2.842	1
$\text{Cs}_2\text{SnI}_6$	Fm3n	4	11.63	-	-	2.849	1
$\text{Rb}_2\text{PbCl}_6$	Fm3n	4	10.197	-	-	2.493	1
$\text{Cs}_2\text{PbCl}_6$	Fm3n	4	10.415	-	-	2.500	1
$(\text{NH}_4)_2\text{PbCl}_6$	Fm3n	4	10.135	-	-	2.483	1
$\text{Rb}_2\text{SbCl}_6$	Fm3n	4	10.14	-	-	-	27
$\text{Rb}_2\text{SeCl}_6$	Fm3n	4	9.978	-	-	2.395	1
$\text{Cs}_2\text{SeCl}_6$	Fm3n	4	10.266	-	-	2.413	1
$(\text{NH}_4)_2\text{SeCl}_6$	Fm3n	4	9.935	-	-	2.384	1
$\text{K}_2\text{SeBr}_6$	Fm3n	4	10.353	-	-	2.539	1
$(\text{NH}_4)_2\text{SeBr}_6$	Fm3n	4	10.46	-	-	2.563	1
$\text{K}_2\text{TeCl}_6$	Fm3n	4	10.143	-	-	-	1
$\text{Rb}_2\text{TeCl}_6$	Fm3n	4	10.233	-	-	2.526	29

continued over

## Results

Table 4.4(ii) continued

Salt	Space group	z	Cell constants (Å)			M-X distance	Ref.
			a	b	c		
Cs <sub>2</sub> GeCl <sub>6</sub>	Fm3n	4	10.21	-	-	2.348	1
K <sub>2</sub> SnCl <sub>6</sub>	Fm3n	4	9.982	-	-	2.411	26
Rb <sub>2</sub> SnCl <sub>6</sub>	Fm3n	4	10.096	-	-	2.422	26
Cs <sub>2</sub> SnCl <sub>6</sub>	Fm3n	4	10.355	-	-	2.423	26
(NH <sub>4</sub> ) <sub>2</sub> SnCl <sub>6</sub>	Fm3n	4	10.044	-	-	2.422	26
Tl <sub>2</sub> SnCl <sub>6</sub>	Fm3n	4	9.97	-	-	2.393	1
Rb <sub>2</sub> SnBr <sub>6</sub>	Fm3n	4	10.64	-	-	2.507	1
Cs <sub>2</sub> SnBr <sub>6</sub>	Fm3n	4	10.81	-	-	2.648	1
(NH <sub>4</sub> ) <sub>2</sub> SnBr <sub>6</sub>	Fm3n	4	10.59	-	-	2.595	1
Rb <sub>2</sub> SnI <sub>6</sub>	Fm3n	4	11.60	-	-	2.842	1
Cs <sub>2</sub> SnI <sub>6</sub>	Fm3n	4	11.63	-	-	2.849	1
Rb <sub>2</sub> PbCl <sub>6</sub>	Fm3n	4	10.197	-	-	2.493	1
Cs <sub>2</sub> PbCl <sub>6</sub>	Fm3n	4	10.415	-	-	2.500	1
(NH <sub>4</sub> ) <sub>2</sub> PbCl <sub>6</sub>	Fm3n	4	10.135	-	-	2.483	1
Rb <sub>2</sub> SbCl <sub>6</sub>	Fm3n	4	10.14	-	-	-	27
Rb <sub>2</sub> SeCl <sub>6</sub>	Fm3n	4	9.978	-	-	2.395	1
Cs <sub>2</sub> SeCl <sub>6</sub>	Fm3n	4	10.266	-	-	2.413	1
(NH <sub>4</sub> ) <sub>2</sub> SeCl <sub>6</sub>	Fm3n	4	9.935	-	-	2.384	1
K <sub>2</sub> SeBr <sub>6</sub>	Fm3n	4	10.363	-	-	2.539	1
(NH <sub>4</sub> ) <sub>2</sub> SeBr <sub>6</sub>	Fm3n	4	10.46	-	-	2.563	1
K <sub>2</sub> TeCl <sub>6</sub>	Fm3n	4	10.143	-	-	-	1
Rb <sub>2</sub> TeCl <sub>6</sub>	Fm3n	4	10.233	-	-	2.526	29

continued over

Results

Table 4.6(ii) continued

Salt	Space group	Cell constants (Å)			d-X distance	Ref.
		z	a	c		
$\text{Cs}_2\text{TeCl}_6$	Fm3n	4	10.447	-	2.507	1
$(\text{NH}_4)_2\text{TeCl}_6$	Fm3n	4	10.200	-	2.528	29
$\text{Ti}_2\text{TeCl}_6$	Fm3n	4	10.107	-	2.476	1
$\text{K}_2\text{TeBr}_6^*$	$P2_1/n$	2	7.521	10.730	2.693	30
$\text{Cs}_2\text{TeBr}_6$	Fm3n	4	10.918	-	2.695	31
$(\text{NH}_4)_2\text{TeBr}_6$	Fm3n	4	10.728	-	2.691	32
$\text{Cs}_2\text{TeI}_6$	Fm3n	4	11.721	-	2.907	1
$(\text{NH}_4)_2\text{TeOCl}_6$	Fm3n	4	10.35	-	2.381	1
$\text{Cs}_2\text{PoBr}_6$	Fm3n	4	11.01	-	2.642	1
$(\text{NH}_4)_2\text{PoBr}_6$	Fm3n	4	10.84	-	2.602	1
$\text{Cs}_2\text{CeCl}_6$	$P3m1$	1	7.476	6.039	2.711	33
$\text{Cs}_2\text{InCl}_6$	$P3m1$	1	7.629	6.050	2.816	1
$\text{Cs}_2\text{LuCl}_6$	$P3m1$	1	7.507	6.050	2.743	1
$\text{Cs}_2\text{PuCl}_6$	$P3m1$	1	7.43	6.03	2.657	1
$\text{Cs}_2\text{BkCl}_6$	$P6_3nc$	2	7.450	12.098	2.550	34

\* presumably a mixture of Sb(III) and Sb(V)

\* monoclinic with  $b=7.5741$ ,  $\beta=89.40^\circ$ 

1. Wyckoff(1965)

2. Siegel(1952)

3. Korol'kov and Efimov(1966)

continued over

Results

Table 4.6(ii) continued

4. Brunton(1973)
5. Lister and Flengas(1964)
6. Eode and Teufer(1956)
7. Gelbman and Westland(1974)
8. Lal and Westland(1974)
9. Brunton(1971)
10. Kennedy and Peacock(1963)
11. Moews(1966)
12. Lalanchette et al(1972)
13. Elder et al(1967)
14. Schwachaw(1964)
15. Peacock(1977)
16. Grundy and Brown(1970)
17. Berthold and Jakobson(1964)
18. Cotton and Johnson(1964)
19. Swanson et al(1963)
20. Swanson et al(1962)
21. Quail and Rivett(1972)
22. Weise and Klemm(1953)
23. Bell et al(1966)
24. Zalkin et al(1964)
25. Haric(1966); Schlemper and Hamilton(1966)
26. Prill et al(1974)

continued over

## Results

Table 4.6(ii) continued

27. Jensen and Rasmussen(1955)
28. Wetster and Collins(1963)
29. Hazell(1966)
30. Brown(1964)
31. Das and Brown(1966)
32. Stepin et al(1968)
33. Kaatz and Marcovich(1966)
34. Morss and Fuger(1965)

computed from the coefficients given in Table 4.6(i) using Equations 4.6(i) and 4.6(iii). The corresponding terms for non-cubic salts are given in Tables 4.6(iii) and 4.6(iv), parameterised as:

$$U_{\text{ELEC}} = \sum_{i=0}^2 C_i q_X^i \quad 4.6(iv)$$

and

$$\left( \frac{\partial U_{\text{ELEC}}}{\partial i} \right)_{i=i_0} = \sum_{j=0}^2 D_{ij} q_X^j \quad 4.6(v)$$

They have been computed using the program MODELING DERIVATIVES (Jenkins and Pratt (1978a)). The model of the anion for the dispersion energy calculations has no viable alternative and is one of six halogen atoms. This model presumably slightly overestimates the dispersion energy by an amount depending on the charge distribution in the anion. However even for small charge distributions the errors should not be great. The ionic polarisabilities of Pirene and Kartheuser (1964) are used throughout and all the other parameters are taken as usual. The results for the dipole-dipole and dipole-quadrupole dispersion energies of the salts are given in Table 4.6(v). The cell length derivatives are not quoted here.

## Results

Table 4.6(iii) Electrostatic energy for non-cubic  
hexahalometallate(IV) salts ( $\text{kJ. mol}^{-1}$ ).

Salt	$C_0$	$C_1$	$C_2$
$\text{K}_2\text{TiF}_6$	1836.4	-73.5	44.8
$\text{K}_2\text{TiF}_6$	1827.5	122.9	-54.5
$\text{Li}_2\text{ZrF}_6$	1847.0	-492.5	29.9
$\text{Rb}_2\text{ZrF}_6$	1693.4	-21.0	-112.2
$\text{Cs}_2\text{ZrF}_6$	1628.0	-24.5	-85.9
$\text{K}_2\text{HfF}_6$	1700.4	-16.2	-111.0
$\text{Cs}_2\text{HfF}_6$	1633.0	-23.1	-85.7
$\text{Li}_2\text{MoF}_6$	2011.0	-206.5	48.1
$\text{K}_2\text{MnF}_6$	1937.6	253.8	-14.0
$\text{Rb}_2\text{MnF}_6$	1889.1	223.7	-7.7
$\text{K}_2\text{ReF}_6$	1779.5	36.1	-80.1
$\text{K}_2\text{RhF}_6$	1823.5	60.9	-109.6
$\text{Rb}_2\text{RhF}_6$	1766.8	50.2	-83.7
$\text{K}_2\text{PtF}_6$	1841.3	211.8	-42.1
$\text{K}_2\text{SiF}_6$	2019.6	-2.1	26.0
$(\text{NH}_4)_2\text{SiF}_6$	1847.3	120.6	-20.2
$\text{K}_2\text{GeF}_6(\text{RT})$	1856.1	100.6	-37.7
$\text{K}_2\text{GeF}_6(\text{HT})$	1940.3	279.5	-3.6
$\text{Rb}_2\text{GeF}_6(\text{FT})$	1789.3	77.6	-30.3
$\text{Rb}_2\text{GeF}_6(\text{HT})$	1865.9	279.3	-3.1

continued over

## Results

Table 4.6(iii) continued

Salt	$C_0$	$C_1$	$C_2$
$(\text{NH}_4)_2\text{CeF}_6$	1781.4	74.1	-29.0
$\text{K}_2\text{TeO}_6$	1516.3	393.3	-56.7
$\text{Cs}_2\text{CeCl}_6$	1421.0	171.6	-73.9
$\text{Cs}_2\text{ThCl}_6$	1394.3	139.3	-106.9
$\text{Cs}_2\text{UCl}_6$	1414.2	121.1	-113.9
$\text{Cs}_2\text{PuCl}_6$	1432.2	166.0	-76.7
$\text{Cs}_2\text{BkCl}_6$	1404.4	293.1	-14.6

Results



Table 4.6(iv) Cell length derivatives of the  
electrostatic energy for non-cubic  
hexahalometallate(IV) salts (kJ.mol<sup>-1</sup>Å<sup>-1</sup>).

Salt	D <sub>a0</sub>	D <sub>a1</sub>	D <sub>a2</sub>	D <sub>o0</sub>	D <sub>o1</sub>	D <sub>o2</sub>
K <sub>2</sub> TiF <sub>6</sub>	-124.2	51.5	-42.6	-135.2	-45.5	-18.9
K <sub>2</sub> TiF <sub>6</sub>	-296.9	-143.9	76.5	29.1	94.4	-0.3
Li <sub>2</sub> ZrF <sub>6</sub>	-136.9	313.6	-87.7	-250.4	136.2	61.7
Li <sub>2</sub> ZrF <sub>6</sub>	-264.6	-212.2	56.8	-13.2	250.8	76.7
Ca <sub>2</sub> ZrF <sub>6</sub>	-245.2	-173.0	36.7	-11.2	206.4	60.6
Li <sub>2</sub> HfF <sub>6</sub>	-265.7	-213.5	57.7	-14.6	248.4	74.5
Ca <sub>2</sub> HfF <sub>6</sub>	-246.4	-174.0	37.0	-11.7	206.3	60.4
Li <sub>2</sub> MoF <sub>6</sub>	-219.0	285.6	16.1	-107.1	-74.3	-59.7
K <sub>2</sub> TaF <sub>6</sub>	-231.8	-123.0	36.1	-66.7	-47.1	-10.7
Rb <sub>2</sub> MnF <sub>6</sub>	-226.9	-110.0	21.7	-59.0	-38.8	-6.8
K <sub>2</sub> ReF <sub>6</sub>	-294.2	-191.2	61.7	-10.9	202.6	45.7
K <sub>2</sub> RhF <sub>6</sub>	-297.7	-248.6	89.5	-25.4	231.5	58.2
Rb <sub>2</sub> RhF <sub>6</sub>	-276.0	-203.9	64.0	-28.8	189.0	45.9
K <sub>2</sub> PtF <sub>6</sub>	-319.7	-176.0	67.4	0.0	64.4	-12.5
Na <sub>2</sub> SiF <sub>6</sub>	-182.8	-48.1	-26.9	-79.2	72.2	1.7
(NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub>	-316.8	-141.4	22.7	-4.7	59.1	7.1
K <sub>2</sub> GeF <sub>6</sub> (RT)	-300.8	-134.8	47.6	-35.6	80.5	8.3
K <sub>2</sub> GeF <sub>6</sub> (HT)	-246.1	-171.4	39.3	-57.7	-32.6	-17.9
Rb <sub>2</sub> GeF <sub>6</sub> (FT)	-279.2	-112.4	34.6	-34.3	73.2	9.1

continued over

results

Table 4.b(iv) continued

Salt	$D_{a0}$	$D_{a1}$	$D_{a2}$	$D_{c0}$	$D_{c1}$	$D_{c2}$
$Rb_2GeF_6(HT)$	-227.5	-156.6	36.3	-53.4	-35.1	-16.6
$(NH_4)_2[GeF_6]$	-279.5	-108.5	32.7	-30.6	73.2	8.9
$K_2TeF_6^*$	-65.7	-75.9	23.4	-49.1	-52.2	22.2
$Cs_2CeCl_6$	-190.8	-169.4	78.3	1.0	106.3	5.2
$Cs_2ThCl_6$	-187.9	-193.4	95.9	5.4	148.6	24.2
$Cs_2UCl_6$	-189.1	-200.4	84.0	0.8	152.3	34.0
$Cs_2PuCl_6$	-193.9	-175.2	71.3	1.5	107.2	11.2
$Cs_2BkCl_6$	-140.1	-112.0	42.7	-36.4	-35.7	-16.2

\* also  $D_{b0} = -65.5$ ,  $D_{b1} = -81.1$ ,  $D_{b2} = 24.0$

## Results

Table 4.6(v) Dispersion energies for hexahalometallate  
(IV) salts ( $\text{kJ}\cdot\text{mol}^{-1}$ ).

Salt	$U_{dd}$	$U_{qd}$	Salt	$U_{dd}$	$U_{qd}$
$\text{Rb}_2\text{TlF}_6$	74	6	$\text{Cs}_2\text{WBr}_6$	152	16
$\text{K}_2\text{TlF}_6$	92	7	$\text{K}_2\text{MnF}_6$	87	7
$\text{K}_2\text{TlCl}_6$	116	10	$\text{Rb}_2\text{MnF}_6(\text{I})$	93	9
$\text{Rb}_2\text{TlCl}_6$	127	11	$\text{Rb}_2\text{MnF}_6(\text{II})$	87	9
$\text{Cs}_2\text{TlCl}_6$	145	15	$\text{Cs}_2\text{MnF}_6$	99	11
$(\text{NH}_4)_2\text{TlCl}_6$	140	15	$\text{K}_2\text{MnCl}_6$	123	10
$\text{Rb}_2\text{TlBr}_6$	155	15	$\text{Rb}_2\text{MnCl}_6$	132	12
$\text{Cs}_2\text{TlBr}_6$	192	20	$(\text{NH}_4)_2\text{MnCl}_6$	136	13
$\text{Li}_2\text{ZrF}_6$	57	4	$\text{K}_2\text{TcCl}_6$	113	9
$\text{Rb}_2\text{ZrF}_6$	86	8	$\text{K}_2\text{ReF}_6$	84	7
$\text{Cs}_2\text{ZrF}_6$	102	12	$\text{K}_2\text{ReCl}_6$	111	9
$\text{Rb}_2\text{ZrCl}_6$	113	10	$\text{K}_2\text{ReBr}_6$	119	10
$\text{Cs}_2\text{ZrCl}_6$	133	14	$\text{K}_2\text{OsCl}_6$	124	10
$\text{Rb}_2\text{HfF}_6$	89	8	$\text{K}_2\text{OsBr}_6$	130	11
$\text{Cs}_2\text{HfF}_6$	104	12	$\text{Rb}_2\text{CoF}_6$	86	8
$\text{Cs}_2\text{CrF}_6$	92	10	$\text{Cs}_2\text{CoF}_6$	98	11
$\text{Li}_2\text{MoF}_6$	50	3	$\text{K}_2\text{RhF}_6$	95	8
$\text{K}_2\text{MoCl}_6$	107	8	$\text{Rb}_2\text{RhF}_6$	102	10
$\text{K}_2\text{HCl}_6$	110	9	$(\text{NH}_4)_2\text{IrCl}_6$	151	15
$\text{Rb}_2\text{HCl}_6$	122	11	$\text{K}_2\text{NiF}_6$	84	7
$\text{Cs}_2\text{HCl}_6$	141	15	$\text{Rb}_2\text{NiF}_6$	96	9
$\text{Rb}_2\text{WBr}_6$	130	11	$(\text{NH}_4)_2\text{PdCl}_6$	138	13

Results

Table 4.6(v) continued

Salt	$U_{dd}$	$U_{qd}$	Salt	$U_{dd}$	$U_{qd}$
$K_2^{2+}F_6$	83	7	$Cs_2GeCl_6$	146	16
$Rb_2^{2+}Cl_6$	119	10	$K_2SnCl_6$	105	9
$Rb_2^{2+}PtCl_6$	129	11	$Pb_2SnCl_6$	119	10
$Cs_2^{2+}PtCl_6$	146	16	$Cs_2SnCl_6$	137	14
$(NH_4)_2^{2+}PtCl_6$	142	13	$(NH_4)_2SnCl_6$	128	12
$Tl_2^{2+}PtCl_6$	247	27	$Tl_2SnCl_6$	224	24
$K_2^{2+}Br_6$	125	11	$Rb_2SnBr_6$	128	11
			$Cs_2SnBr_6$	154	16
$Rb_2SiF_6$	65	5	$(NH_4)_2SnBr_6$	136	13
$K_2SiF_6$	81	6	$Rb_2SnI_6$	126	11
$Rb_2SiF_6$	86	8	$Cs_2SnI_6$	154	16
$Cs_2SiF_6$	93	11	$Pb_2PbCl_6$	115	12
$(NH_4)_2SiF_6(I)$	55	6	$Cs_2PbCl_6$	136	14
$(NH_4)_2SiF_6(II)$	96	9	$(NH_4)_2PbCl_6$	125	11
$Tl_2SiF_6$	173	20	$Rb_2SeCl_6$	127	11
$K_2GeF_6(RT)$	90	7	$Cs_2SeCl_6$	145	15
$K_2GeF_6(HT)$	87	7	$(NH_4)_2SeCl_6$	136	13
$Rb_2GeF_6(RT)$	97	9	$K_2SeBr_6$	127	11
$Rb_2GeF_6(HT)$	94	9	$(NH_4)_2SeBr_6$	147	14
$Cs_2GeF_6$	93	11	$Rb_2TeCl_6$	115	12
$(NH_4)_2GeF_6(I)$	101	10	$Cs_2TeCl_6$	132	13
$(NH_4)_2GeF_6(II)$	92	9	$(NH_4)_2TeCl_6$	122	11

continued over

Results

Table 4.6(v) continued

Salt	$U_{dd}$	$U_{qd}$	Salt	$U_{dd}$	$U_{qd}$
$Tl_2TeCl_6$	211	22	$(NH_4)_2PoBr_6$	114	17
$K_2TeBr_6$	112	10			
$Cs_2TeBr_6$	147	15	$Cs_2CeCl_6$	141	15
$(NH_4)_2TeBr_6$	132	12	$Cs_2ThCl_6$	136	14
$Cs_2TeI_6$	152	15	$Cs_2UCl_6$	142	15
$(NH_4)_2PoCl_6$	100	8	$Cs_2PuCl_6$	141	15
$Cs_2PoBr_6$	134	13	$Cs_2BkCl_6$	131	13

Results

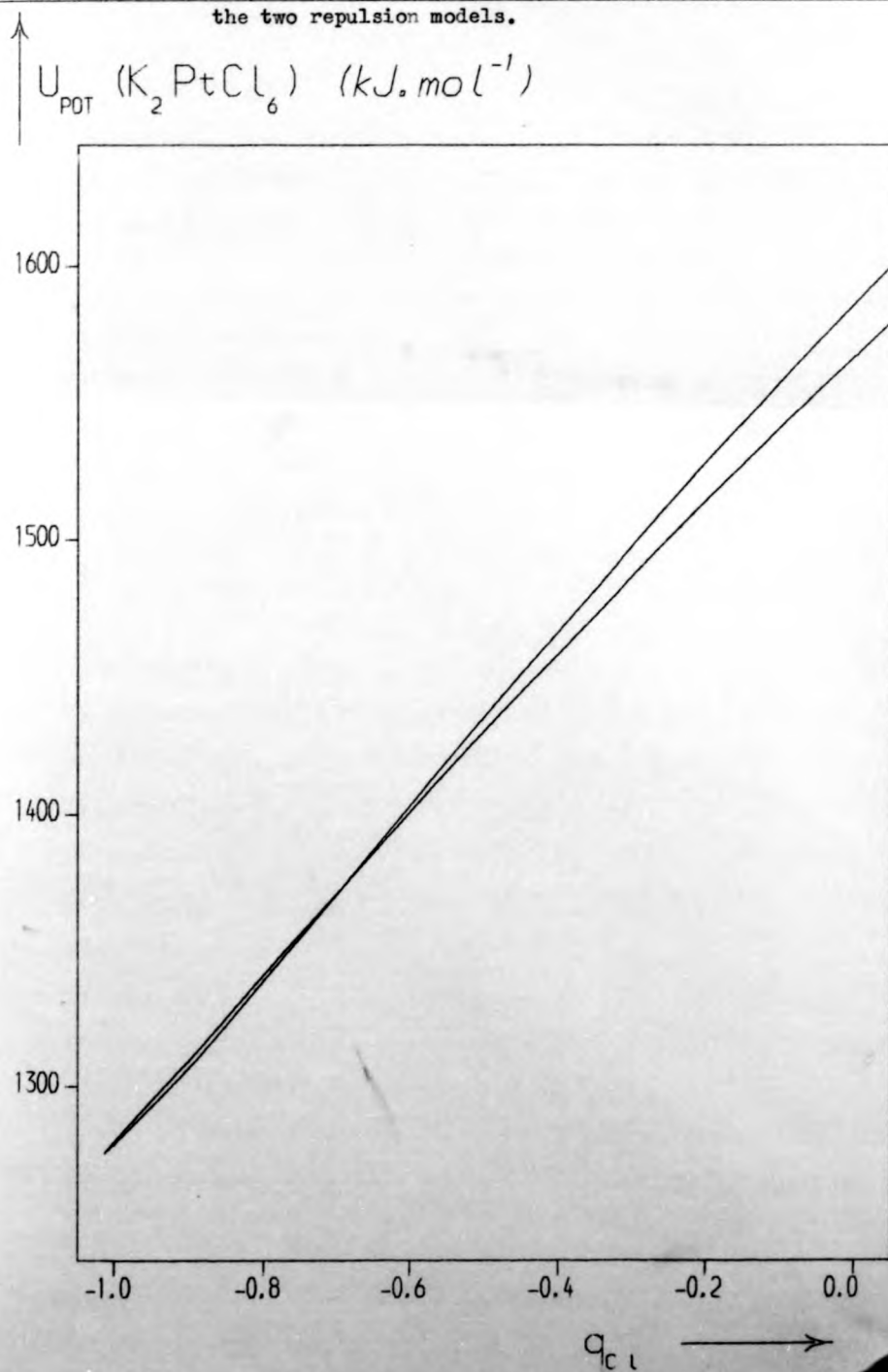
A repulsion model for the hexahalometallate(IV) ions has to be assigned. The ions could be considered as spherical, i.e. a model of a single sphere centered on the metal. This has the advantages that it assigns an overall basic radius to the ion, giving an idea of its relative size and repulsion properties, and ease of computation. For the salts possessing the anti-fluorite potassium hexachloroplatinate structure this model appears reasonable in the sense that it yields approximately equivalent results to those given by the six sphere model discussed next. This near equivalence is shown by the plot of the lattice energy of potassium hexachloroplatinate versus charge on the chlorine atoms for the two models, shown in Figure 4.6(i). The one sphere model (leading to the lower of the two curves) is used for all salts with the anti-fluorite structure.

For salts possessing non-cubic structures the one sphere approximation is not such a good one (see Section 2.8). So a model of six spheres centered on the halogen atoms of the ion is adopted in these cases. The form of the Huggins and Mayer repulsion energy equation for this model is:

$$U_R = 6rc_m \exp\left(\frac{2\bar{r}_m}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{mi}}{\rho}\right) + 26rc_m \exp\left(\frac{\bar{r}_m + \bar{r}_s}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{si}}{\rho}\right) + 36rc_m \exp\left(\frac{2\bar{r}_s}{\rho}\right) \sum_i^{\text{ions}} \exp\left(-\frac{R_{si}}{\rho}\right) \quad 4.6(v1)$$

Results

Figure 4.6(i) Lattice energy of potassium hexachloroplatinate for the two repulsion models.



where all the terms are defined under previous equations. The one sphere model is however also adopted in order to obtain values for the approximate quantity of the basic radius of the anion.

Aside from the basic radius assigned to the anion, or parts of it, another parameter not known experimentally is the charge distribution in the anion. A distribution of the form:

$$q_M + 6 q_X = -2 \quad 4.6(vii)$$

completely analogous to Equation 4.6(ii) is assumed. In the case of salts with non-cubic symmetry the charge distribution can usually be obtained by intersection between curves resulting from differentiation with respect to the different unit cell sides. In only a few cases is that not possible here. However for cubic salts there is only one curve, hence no possibility of intersection and so a value has to be assigned in order to obtain lattice energy and thermochemical results. There are three possible mechanisms for the assignment.

(a) A value can be obtained from calculation on other salts of the same anion. For this to be possible a

#### Results



non-cubic salt has to be available. Ideally it should be possible to assign a value from two or more salts with a common anion by intersection of curves of basic radii against charge on the halogen atom, however these curves are so similar in form for all cubic salts (Jenkins and Pratt (1976c)) that intersection cannot be relied on without a non-cubic salt as a discriminant.

(b) Nuclear quadrupole resonance studies provide an experimental method of estimating the charge distribution. However the literature only contains results for a few anions, mainly involving main group metals.

(c) Failing (a) and (b) it is necessary to estimate a value. Jorgensen (1962, 1963, 1967) and co-workers (Jorgensen, Horner, Hatfield and Tyree (1957)) have proposed a method for estimating charge distributions in complex ions, which uses differential ionisation energies as a measure of electronegativity. A simple method was supposedly improved by a 'Madelung correction' however it is found that an average of the two methods gives much better, and consistent, agreement with the experimentally determined values. This calculational approach is used if no value can otherwise be estimated.

The two publications (Jenkins and Pratt (1978c,c)) contain a plethora of figures showing the basic radii,

#### Results

lattice energy and thermochemical function graphs for the many salts considered. They are not included here as the duplication and bulk is not considered justified by the information contained. The results for the charge distributions, basic radii and lattice energies arising from each salt are given in Table 4.6(vi), together with an indication of the source of the charge distribution value. The table is felt to give sufficient information for the purposes of this account.

It was found in the study of salts with cubic symmetry that, when X was chlorine and where sufficient data existed, the calculated lattice energy had an approximately linear dependence on the cubic cell side for constant cation, especially for larger cell sides. By fitting the results the following approximate equalities were obtained:

$$U_{\text{POT}}(\text{K}_2\text{MCl}_6) = -329 a_0 + 4655 \text{ kJ.mol}^{-1} \quad 4.6(\text{viii})$$

$$U_{\text{POT}}(\text{Rb}_2\text{MCl}_6) = -339 a_0 + 4795 \text{ kJ.mol}^{-1} \quad 4.6(\text{ix})$$

$$U_{\text{POT}}(\text{Cs}_2\text{MCl}_6) = -348 a_0 + 4969 \text{ kJ.mol}^{-1} \quad 4.6(\text{x})$$

$$U_{\text{POT}}((\text{NH}_4)_2\text{MCl}_6) = -309 a_0 + 4486 \text{ kJ.mol}^{-1} \quad 4.6(\text{xi})$$

These can be used to obtain lattice energies for

#### Results

Table 4.6(vi) Calculated lattice energies for  
hexahalometallate(IV) salts.

Salt	$\alpha_X$	Source	$r_{MX_6}^{2-}(\text{\AA})$	$U_{POT}^{(1)}$ (kJ.mol <sup>-1</sup> )
$Na_2TiF_6$	-0.42	a	-	1687
$K_2TiF_6$	-0.73	a	2.21	1617
$K_2TiCl_6$	-0.61	b	2.48	1417
$Rb_2TiCl_6$	-0.61	b	2.47	1415
$Cs_2TiCl_6$	-0.61	b	2.50	1407
$(NH_4)_2TiCl_6$	-0.61	b	2.50	1417
$Rb_2TiBr_6$	-0.59	b	2.62	1349
$Cs_2TiBr_6$	-0.59	b	2.61	1337
$Li_2ZrF_6$	-0.90	a	2.52	1965
$Rb_2ZrF_6$	-0.42	a	2.32	1587
$Cs_2ZrF_6$	-0.46	a	2.34	1537
$Rb_2ZrCl_6$	-0.66	b	2.45	1349
$Cs_2ZrCl_6$	-0.66	b	2.49	1349
$Rb_2HfF_6$	-0.44	a	2.30	1589
$Cs_2HfF_6$	-0.46	a	2.33	1549
$Cs_2CrF_6$	-0.65	b	2.08	1607
$Li_2MoF_6$	-0.33	a	2.44	1877
$K_2UOCl_6$	-0.60	b	2.54	1419
$K_2HfCl_6$	-0.62	c	2.50	1399
$Rb_2HfCl_6$	-0.62	c	2.47	1397
$Cs_2HfCl_6$	-0.62	c	2.51	1392

continued over

Results

Table 4.6(vi) continued

Salt	$\alpha_X$	Source	$r_{MX_6}^{2-9}$ (Å)	$U_{pot}^{2-9}$ (kJ. mol <sup>-1</sup> )
Rb <sub>2</sub> WBr <sub>6</sub>	-0.55	d	2.73	136 <sup>1</sup>
Cs <sub>2</sub> WBr <sub>6</sub>	-0.55	d	2.72	136 <sup>2</sup>
K <sub>2</sub> MnF <sub>6</sub>	-0.95	a	1.96	163 <sup>2</sup>
Rb <sub>2</sub> MnF <sub>6</sub> (I)	-1.12	a	1.87	158 <sup>2</sup>
Rb <sub>2</sub> MnF <sub>6</sub> (II)*	-0.63	b	1.99	168 <sup>9</sup>
Cs <sub>2</sub> MnF <sub>6</sub> *	-0.63	b	2.05	162 <sup>2</sup>
K <sub>2</sub> MnCl <sub>6</sub>	-0.55	b	2.51	146 <sup>2</sup>
Rb <sub>2</sub> MnCl <sub>6</sub>	-0.55	b	2.50	145 <sup>1</sup>
(NH <sub>4</sub> ) <sub>2</sub> MnCl <sub>6</sub>	-0.55	b	2.56	146 <sup>4</sup>
K <sub>2</sub> TcCl <sub>6</sub>	-0.49	b	2.59	144 <sup>2</sup>
K <sub>2</sub> ReF <sub>6</sub>	-0.56	a	2.26	162 <sup>2</sup>
K <sub>2</sub> ReCl <sub>6</sub>	-0.56	c	2.54	141 <sup>5</sup>
K <sub>2</sub> ReBr <sub>6</sub>	-0.5	d	2.81	137 <sup>5</sup>
K <sub>2</sub> OsCl <sub>6</sub>	-0.51	c	2.54	144 <sup>7</sup>
K <sub>2</sub> OsBr <sub>6</sub>	-0.45	d	2.80	139 <sup>6</sup>
Rb <sub>2</sub> CoF <sub>6</sub>	-0.59	b	2.00	168 <sup>9</sup>
Cs <sub>2</sub> CoF <sub>6</sub>	-0.59	b	2.07	163 <sup>2</sup>
K <sub>2</sub> RhF <sub>6</sub>	-0.40	a	2.23	166 <sup>8</sup>
Rb <sub>2</sub> RhF <sub>6</sub>	-0.43	a	2.23	162 <sup>6</sup>
(NH <sub>4</sub> ) <sub>2</sub> IrCl <sub>6</sub>	-0.47	c	2.56	144 <sup>2</sup>
K <sub>2</sub> NiF <sub>6</sub>	-0.57	b	1.94	172 <sup>1</sup>
Rb <sub>2</sub> NiF <sub>6</sub>	-0.57	b	2.01	168 <sup>9</sup>

continued over

Results

Table 4.6(vi) continued

Salt	$\alpha_X$	Source	$\bar{r}_{MX_6}^{2-}(\text{\AA})$	$U_{POT}^{2-1}$ (kJ.mol <sup>-1</sup> )
(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>6</sub>	-0.43	e	2.61	1481
K <sub>2</sub> PtF <sub>6</sub>	-0.86	a	2.15	1561
K <sub>2</sub> PtCl <sub>6</sub>	-0.44	e	2.60	1468
Pb <sub>2</sub> PtCl <sub>6</sub>	-0.44	e	2.56	1464
Cs <sub>2</sub> PtCl <sub>6</sub>	-0.44	e	2.58	1444
(NH <sub>4</sub> ) <sub>2</sub> IrCl <sub>6</sub>	-0.44	e	2.62	1468
Tl <sub>2</sub> PtCl <sub>6</sub>	-0.44	e	2.60	1545
K <sub>2</sub> PtBr <sub>6</sub>	-0.39	e	2.85	1423
Na <sub>2</sub> SrF <sub>6</sub>	-0.63	a	2.33	1831
K <sub>2</sub> SrF <sub>6</sub>	-0.64	b	1.79	1671
Rb <sub>2</sub> SrF <sub>6</sub>	-0.84	b	1.87	1639
Cs <sub>2</sub> SrF <sub>6</sub>	-0.84	b	2.01	1604
(NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> (I)	-0.93	a	2.04	1615
(NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> (II)	-0.84	b	1.96	1655
Tl <sub>2</sub> SiF <sub>6</sub>	-0.84	b	2.05	1675
K <sub>2</sub> GeF <sub>6</sub> (RT)	-0.75	a	2.17	1655
K <sub>2</sub> GeF <sub>6</sub> (HT)	-0.40	a	2.04	1718
Pb <sub>2</sub> GeF <sub>6</sub> (RT)	-0.77	a	2.18	1614
Rb <sub>2</sub> GeF <sub>6</sub> (HT)	-0.41	a	2.03	1649
Cs <sub>2</sub> GeF <sub>6</sub>	-0.78	b	2.02	1571
(NH <sub>4</sub> ) <sub>2</sub> GeF <sub>6</sub> (I)	-0.86	a	2.23	1607

continued over

Results

Table 4.6(vi) continued

Salt	$\chi$	Source	$r_{MX_6}^{2-}(\text{\AA})$	$U_{POT}^{2-}(\text{kJ.mol}^{-1})$
$(\text{NH}_4)_2\text{GeF}_6$ (II)	-0.78	b	1.99	1657
$\text{Cs}_2\text{GeCl}_6$	-0.73	b	2.43	1375
$\text{K}_2\text{SnCl}_6$	-0.66	e	2.45	1363
$\text{Rb}_2\text{SnCl}_6$	-0.66	e	2.43	1361
$\text{Cs}_2\text{SnCl}_6$	-0.66	e	2.48	1358
$(\text{NH}_4)_2\text{SnCl}_6$	-0.66	e	2.48	1370
$\text{Ti}_2\text{SnCl}_6$	-0.66	e	2.55	1437
$\text{Rb}_2\text{SnBr}_6$	-0.60	e	2.69	1309
$\text{Cs}_2\text{SnBr}_6$	-0.60	e	2.67	1306
$(\text{NH}_4)_2\text{SnBr}_6$	-0.60	e	2.74	1319
$\text{Rb}_2\text{SnI}_6$	-0.55	e	3.11	1226
$\text{Cs}_2\text{SnI}_6$	-0.55	e	3.03	1243
$\text{Rb}_2\text{PbCl}_6$	-0.63	e	2.45	1343
$\text{Cs}_2\text{PbCl}_6$	-0.63	e	2.48	1344
$(\text{NH}_4)_2\text{PbCl}_6$	-0.63	e	2.50	1355
$\text{Rb}_2\text{SeCl}_6$	-0.56	e	2.50	1409
$\text{Cs}_2\text{SeCl}_6$	-0.56	e	2.52	1397
$(\text{NH}_4)_2\text{SeCl}_6$	-0.56	e	2.55	1420
$\text{K}_2\text{SeBr}_6$	-0.47	e	2.81	1379
$(\text{NH}_4)_2\text{SeBr}_6$	-0.47	e	2.81	1380
$\text{Rb}_2\text{TeCl}_6$	-0.68	e	2.35	1316
$\text{Cs}_2\text{TeCl}_6$	-0.68	e	2.44	1323

continued over

Results

Table 4.6(vi) continued

Salt	$\alpha_X$	Source	$\bar{r}_{MX_6}^{2-}(\text{\AA})$	$U_{FOT}^{2-}$ (kJ.mol <sup>-1</sup> )
(NH <sub>4</sub> ) <sub>2</sub> TeCl <sub>6</sub>	-0.68	e	2.41	1327
Tl <sub>2</sub> TeCl <sub>6</sub>	-0.68	e	2.54	1392
K <sub>2</sub> TeBr <sub>6</sub>	-0.56	a	2.86	1297
Cs <sub>2</sub> TeBr <sub>6</sub>	-0.58	e	2.70	1277
(NH <sub>4</sub> ) <sub>2</sub> TeBr <sub>6</sub>	-0.53	e	2.76	1294
Cs <sub>2</sub> TeI <sub>6</sub>	-0.48	e	3.10	1246
(NH <sub>4</sub> ) <sub>2</sub> TeOCl <sub>6</sub>	-0.7	f	2.60	1339
Cs <sub>2</sub> TeOBr <sub>6</sub>	-0.6	f	2.74	1286
(NH <sub>4</sub> ) <sub>2</sub> TeOBr <sub>6</sub>	-0.6	f	2.83	1297
Cs <sub>2</sub> CeCl <sub>6</sub>	-0.52	a	2.90	1317
Cs <sub>2</sub> ThCl <sub>6</sub>	-0.42	a	2.94	1315
Cs <sub>2</sub> UCl <sub>6</sub>	-0.34	a	2.92	1352
Cs <sub>2</sub> PuCl <sub>6</sub>	-0.49	a	2.87	1331
Cs <sub>2</sub> BkCl <sub>6</sub>	-0.69	a	2.70	1295

\* -0.63 preferred to maintain general trends

a assigned from intersection of curves

b estimated from the work of Jorgensen (see text)

c Brown, McDougale and Kent(1970)

d estimated from the result for  $\text{MCl}_6^{2-}$

e Kubo and Nakamura(1966)

f estimated from other results

#### Results

salts where only the cubic cell side is known experimentally, and so the full calculations cannot be performed. The results found, using the crystal structure data contained in table 4.6(i), are given in Table 4.6(vii).

The thermochemical cycle which relates the lattice enthalpy to the enthalpies of formation of the gaseous ions produces the equality:

$$\Delta H_f^\circ(MX_6^{2-})(g) = U_{POT}(A_2MX_6) + \Delta H_f^\circ(A_2MX_6)(c) - 2\Delta H_f^\circ(M^+)(g) + nRT \quad 4.6(xii)$$

where  $n=0$  for monatomic  $M$  and  $n=3$  for ammonium.

The paucity of thermochemical data for these salts allows Equation 4.6(xii) to be applied in only some cases, and this is an unfortunate property of this system. However it is an indication of the difficulties inherent in making the determination of thermochemical properties of these salts which makes this study of importance as a review of the available data and as a guideline to the thermodynamics of these systems. The available enthalpies of formation of crystalline salts included in this study are given in Table 4.6(viii) along with the value of the

#### Results



Table 4.6(vii) Lattice energies of further hexahalometallate(IV) salts estimated by Equations 4.6(viii)-4.6(xi) ( $\text{kJ. mol}^{-1}$ ).

Salt	$U_{\text{POT}}$	Salt	$U_{\text{POT}}$
$\text{K}_2\text{ZrCl}_6$	1339	$\text{Rb}_2\text{ReCl}_6$	1414
$\text{K}_2\text{HfCl}_6$	1345	$\text{Cs}_2\text{ReCl}_6$	1399
$\text{K}_2\text{NbCl}_6$	1375	$(\text{NH}_4)_2\text{ReCl}_6$	1402
$\text{Rb}_2\text{NbCl}_6$	1371	$\text{K}_2\text{RuCl}_6$	1451
$\text{Cs}_2\text{NbCl}_6$	1381	$\text{Cs}_2\text{OsCl}_6$	1409
$\text{K}_2\text{TaCl}_6$	1378	$(\text{NH}_4)_2\text{OsCl}_6$	1433
$\text{Rb}_2\text{TaCl}_6$	1368	$\text{K}_2\text{PtCl}_6$	1459
$\text{Cs}_2\text{TaCl}_6$	1378	$\text{Rb}_2\text{PtCl}_6$	1449
$\text{Rb}_2\text{MoCl}_6$	1408	$\text{Cs}_2\text{PtCl}_6$	1425
$\text{Cs}_2\text{MoCl}_6$	1395		
$\text{Cs}_2\text{MnCl}_6$	1430	$\text{Rh}_2\text{SbCl}_6$	1357
$\text{Rb}_2\text{TeCl}_6$	1417	$\text{K}_2\text{TeCl}_6$	1319

## Results

Table 4.6(viii) Enthalpies of formation of gaseous  
hexahalometallate(IV) ions ( $\text{kJ. mol}^{-1}$ ).

Salt	$\Delta H_f^\circ(\text{AX}_6)$	Source	$\Delta H_f^\circ(\text{MX}_6^{2-})$
$\text{K}_2\text{TlF}_6$	-2910	Ramburov (1963)	-2321
$\text{Rb}_2\text{TiCl}_6$	-1747a	Kecrolovskov and	-1361
$\text{Rb}_2\text{TiCl}_6$	-1767a	Efimov (1966)	-1342
$\text{Cs}_2\text{TiCl}_6$	-1797a		-1300
$\text{Rb}_2\text{TiBr}_6$	-1517a		-1166
$\text{Cs}_2\text{TiBr}_6$	-1553a		-1119
$\text{K}_2\text{ZrCl}_6$	-1932	Gelbman and	-1621b
$\text{Cs}_2\text{ZrCl}_6$	-1992	Westland (1974)	-1549
$\text{K}_2\text{HfCl}_6$	-1957		-1640b
$\text{K}_2\text{MoCl}_6$	-1594	Lal and	-1247b
$\text{Rb}_2\text{NbCl}_6$	-1619	Westland (1974)	-1238b
$\text{Cs}_2\text{NbCl}_6$	-1663		-1187b
$\text{K}_2\text{TaCl}_6$	-1648		-1298b
$\text{Rb}_2\text{TaCl}_6$	-1669		-1291b
$\text{Cs}_2\text{TaCl}_6$	-1711		-1238b
$\text{K}_2\text{MoCl}_6$	-1475	Barnes et al (1974)	-1085
$\text{Rb}_2\text{MoCl}_6$	-1495	Efimov and	-1077b
$\text{Cs}_2\text{MoCl}_6$	-1527	Beloruka (1967)	-1037b
$\text{K}_2\text{WCl}_6$	-1380	Peacock (1977)	-1010
$\text{Rb}_2\text{WCl}_6$	-1429	Barnes et al (1974)	-1022
$\text{Cs}_2\text{WCl}_6$	-1446		-959

continued over

Results

Table 4.6(viii) continued

Salt	$\Delta H_f^\circ(A_2MX_6)$ (cal)	Source	$\Delta H_f^\circ(MX_2)$ (cal)
$RL_2WBr_6$	-1126	Peacock(1977)	-735
$Cs_2WBr_6$	-1132	Peacock(1977)	-675
$K_2TeCl_6$	-1333	Wagman et al(1969)	-945
$(NH_4)_2TeCl_6$	-1057	Glyshko(1974)	-915h
$K_2ReBr_6$	-1036	Peacock(1977)	-689
$K_2OsCl_6$	-1171	Rossini et al(1952)	-752
$K_2IrCl_6$	-1197		-785c
$K_2VIF_6$	-2021	Hopkins(1970)	-1328
$K_2PdCl_6$	-1187	Rossini et al(1952)	-734c
$K_2PtCl_6$	-1237	Caulter et al(1940)	-797
$(NH_4)_2PtCl_6$	-994	Shidlovskii et al('61)	-786
$K_2PtBr_6$	-1040	Rossini et al(1952)	-645
$Na_2SiF_6$	-2910	Wagman et al(1976)	-2300
$K_2SiF_6$	-2966		-2324
$RL_2SiF_6$	-2919		-2270
$Cs_2SiF_6$	-2801	Rossini et al(1952)	-2102
$(NH_4)_2SiF_6(I)$	-2681	Wagman et al(1968)	-2326
$(NH_4)_2SiF_6(II)$	-2682		-2277
$K_2GeF_6(RT)$	-2600	Hopkins(1970)	-1973
$Cs_2GeCl_6$	-1452	Welsh et al(1974)	-981
$K_2SnCl_6$	-1485		-1150

continued over

Results

Table 4.6(viii) continued

Salt	$\Delta H_f^\circ (MX_6)$	Source	$\Delta H_f^\circ (MX_6^{2-})$
$Hg_2SnCl_6$	-1529	Webster & Collins(1963)	-1158
$(NH_4)_2SnCl_6$	-1237	Wagman et al(1968)	-1127
$Hg_2PbCl_6$	-1293	Welsh et al(1974)	-940
$Hg_2TeCl_6$	-1167	Golutvin et al(1974)	-877b
$Hg_2TeCl_6$	-1251		-925
$Hg_2TeBr_6$	-972	Stepin et al(1968)	-703
$Cs_2TeBr_6$	-1032		-645
$Cs_2ThCl_6$	-2128	Fuger and Brown(1971)	-1718
$Cs_2UCl_6$	-2018	Vdovenko et al(1974)	-1571
$Cs_2PuCl_6$	-1954	Fuger and Brown(1971)	-1527

a quoted from gaseous atoms, converted to an enthalpy of formation from standard states

b obtained via an estimated lattice energy

c using the empirical relationship  $U_{POT}(K_2MCl_6) = U_{POT}((NH_4)_2MCl_6)$  which is found for cubic salts

## Results

enthalpy of formation of the gaseous hexahalometallate(IV) ion found from the above equation. The subsidiary data concerning the enthalpies of formation of the gaseous cations is as was used for the hexafluoride ion (Table 4.5(v)).

In Table 4.6(viii) the results obtained from cesium salts are invariably lower than those from other salts of the same anion. This could well be caused by the same thermochemical source of error alluded to in Section 4.5 and so values obtained from calculations on cesium salts are omitted where others can be taken. The final thermochemical results are given in Table 4.6(ix). Trends between values are much the same as expected.

The absolute hydration enthalpy of the anions can be estimated in a few cases from the above results using the relationship:

$$\Delta H_{\text{hyd}}^{\circ}(\text{MX}_6^{2-})(g) = \Delta H_f^{\circ}(\text{MX}_6^{2-})(aq) - \Delta H_f^{\circ}(\text{MX}_6^{2-})(g) - 2\Delta H_f^{\circ}(\text{H}^+)(g) - 2\Delta H_{\text{hyd}}^{\circ}(\text{H}^+)(g) \quad 4.6(\text{xi})$$

The results obtained are listed in Table 4.6(ix), incorporating the data  $\Delta H_f^{\circ}(\text{H}^+)(g) = 1536.2 \text{ kJ.mol}^{-1}$  (Wagman et al (1968)) and  $\Delta H_{\text{hyd}}^{\circ}(\text{H}^+)(g) = -1100.6 \text{ kJ.mol}^{-1}$

## Results

Table 4.6(ix) Thermochemical results and bond energies  
for hexahalometallate(IV) ions ( $\text{kJ.mol}^{-1}$ ).

Ion	$\Delta H_f^\circ$ ( $\text{MX}_6^{2-}$ ) (g)	$\Delta H_f^\circ$ ( $\text{MX}_6^{2-}$ ) (g)	$\overline{E}(\text{M-X})$ hom	$\overline{E}(\text{M-X})$ het	cbe (eV)
$\text{TiF}_6^{2-}$	-2321	-	544	1692	105.2
$\text{TiCl}_6^{2-}$	-1352	-	418	1538	95.6
$\text{TiBr}_6^{2-}$	-1166	-	376	1521	94.6
$\text{ZrCl}_6^{2-}$	-1585	-	467	1365	84.9
$\text{HfCl}_6^{2-}$	-1640	-	498	1336	83.1
$\text{NbCl}_6^{2-}$	-1243	-	443	1458	90.7
$\text{TaCl}_6^{2-}$	-1295	-	461	1385	86.1
$\text{MoCl}_6^{2-}$	-1081	-	407	1618	100.6
$\text{WCl}_6^{2-}$	-1016	-	422	1438	89.4
$\text{HfBr}_6^{2-}$	-735	-	366	1406	87.4
$\text{FeCl}_6^{2-}$	-945	-663	399	1479	92.0
$\text{ReBr}_6^{2-}$	-689	-	355	1460	90.8
$\text{OsCl}_6^{2-}$	-752	-	378	1496	93.0
$\text{IrCl}_6^{2-}$	-785	-706	363	1478	91.9
$\text{NiF}_6^{2-}$	-1328	-	372	1933	120.2
$\text{RuCl}_6^{2-}$	-734	-735	309	1723	107.1
$\text{PtCl}_6^{2-}$	-792	-757	348	1577	98.0
$\text{PtBr}_6^{2-}$	-645	-703	313	1567	97.4
$\text{SiF}_6^{2-}$	-2299	-961	530	1869	116.2

continued over

Results

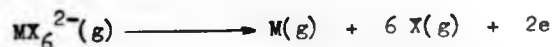
Table 4.6(ix) continued

Ion	$\Delta H_f^\circ$ (MX <sub>6</sub> ) <sup>2-</sup> (gf)	$\Delta H_f^\circ$ (MX <sub>6</sub> ) <sup>2-</sup> (q)	$\overline{E(M-X)}$ hom	$\overline{E(M-X)}$ het	cbe (eV)
GeF <sub>6</sub> <sup>2-</sup>	-1973	-	470	1821	113.2
GeCl <sub>6</sub> <sup>2-</sup>	-981	-	348	1672	104.0
SnCl <sub>6</sub> <sup>2-</sup>	-1145	-696	367	1521	94.5
PuCl <sub>6</sub> <sup>2-</sup>	-940	-	311	1518	94.4
TeCl <sub>6</sub> <sup>2-</sup>	-925	-	296	1510	93.9
TeBr <sub>6</sub> <sup>2-</sup>	-703	-	248	1486	92.4
TnCl <sub>6</sub> <sup>2-</sup>	-1718	-	507	1357	84.4
UCl <sub>6</sub> <sup>2-</sup>	-1571	-	464	-	-
PuCl <sub>6</sub> <sup>2-</sup>	-1527	-	434	-	-

Results

(Jenkins and Morris (1976)).

The bond energy of hexahalometallate ions can be defined in two ways. The first is with respect to homolytic fission of the bonds:

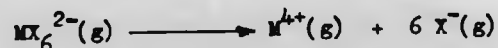


where one sixth of the enthalpy change of this above reaction can be described as the homolytic bond energy,  $\overline{E(\text{M-X})}_{\text{hom}}$  correspondingly:

$$\overline{E(\text{M-X})}_{\text{hom}} = \frac{1}{6} \left[ -\Delta H_f^\circ(\text{MX}_6^{2-})(\text{g}) + \Delta H_{\text{sub}}^\circ(\text{M})(\text{c}) + 3D_{\text{X}_2} \right] \quad 4.6(\text{xiv})$$

where the second and third terms on the right-hand side of this equation are the enthalpy of sublimation of the metal and the dissociation enthalpy of the halogen respectively. This definition is more applicable at high temperatures.

The second definition refers to heterolytic fission of the bonds:



## Results



where one sixth of the enthalpy change of this process is referred to as the heterolytic bond energy,  $\overline{E(M-X)}_{het}$ , where:

$$\overline{E(M-X)}_{het} = \frac{1}{6} \left[ -\Delta H_f^\circ(MX_6^{2-})(g) + \Delta H_f^\circ(M^{4+})(g) + 6\Delta H_f^\circ(X^-)(g) \right] \quad 4.6(xv)$$

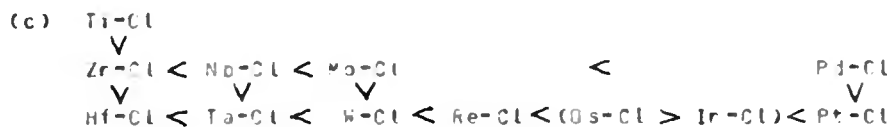
This definition has been generally selected (see Basolo and Pearson (1958)) for use as a better guide to properties of the ions. Basolo and Pearson quote their 'coordinate bond energy' (cbe), in electron volts, as six times the heterolytic bond energy.

Using data from standard thermochemical tables and the results for the enthalpy of formation of the gaseous anions we obtain the bond energy results given in Table 4.6(ix).

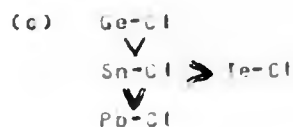
The results for the heterolytic bond energy can be summarised by the following trends which are similar to those that could be predicted from simple chemical considerations. The symbol 'M-X' symbolises the bond energy.

- (a)  $M-F > M-Cl > M-Br$
- (b)  $Si-F > Ge-F$

#### Results

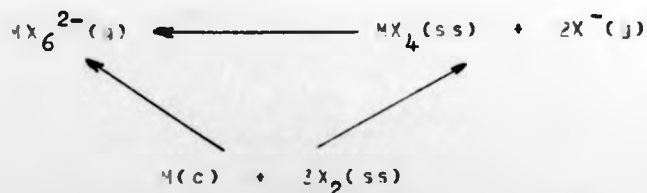


where the brackets indicate that the somewhat spurious order here could result from the fact that these are only estimated quantities.



Consideration of the homolytic bond energies leads to almost complete reversal of these trends.

The thermochemical cycle:

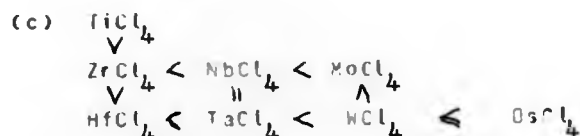
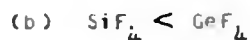


where ss refers to standard state, leads to the expression for the double halide ion affinity of the tetrahalide molecule,  $\overline{\Delta H}_X(ss)$ , to be:

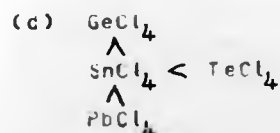
$$\overline{\Delta H}_X(ss) = \Delta H_f^\circ(MX_6^{2-})(g) - \Delta H_f^\circ(MX_4)(ss) - 2\Delta H_f^\circ(X^-)(g) \quad 4.6(xvi)$$

## Results

The most useful of these commodities is where  $ss=q$ . Using the data (Cox et al (1972))  $\Delta H_f^\circ(F^-)(g) = -270.7$ ,  $\Delta H_f^\circ(Cl^-)(g) = -246.0$  and  $\Delta H_f^\circ(Br^-)(g) = -233.9 \text{ kJ.mol}^{-1}$  we generate the halide ion affinities given in Table 4.6(x). In considering the cases for the gaseous metal tetrahalides we find the trends, where  $MX_4$  refers to the gaseous double halide ion affinity, showing:



an interesting reversal in vertical trends over the first three groups.



which shows the opposite vertical trend to the titanium group and confirms the reversal shown by the molybdenum (chromium) group. The 'right greater than left' trend is observed across the periodic table.

Other literature values for the lattice energies and

## Results

Table 4.6(x) Double halide ion affinities for metal tetrahalides ( $\text{kJ}\cdot\text{mol}^{-1}$ ).

Molecule	ss	$\Delta H_f^\circ(\text{MX}_4)(\text{ss})$	Source	$\Delta H_x^\circ(\text{ss})$
$\text{TiF}_4$	g	-1552	a	-228
	c	-1649	a	-130
$\text{TiCl}_4$	g	-763	a	-98
	l	-804	a	-58
$\text{TiBr}_4$	g	-549	a	-149
	c	-617	a	-82
$\text{ZrCl}_4$	g	-870	a	-223
	c	-981	a	-113
$\text{HfCl}_4$	g	-889	a	-259
	c	-990	a	-158
$\text{NbCl}_4$	g	-561	b	-190
	c	-694	b	-57
$\text{TaCl}_4$	g	-561	b	-242
	c	-702	b	-102
$\text{MoCl}_4$	g	-386	c	-203
	c	-476	c	-113
$\text{WCl}_4$	g	-341	c	-185
	c	-447	c	-77
$\text{WBr}_4$	c	-146	d	-121
$\text{ReCl}_4$	c	-361	e	-92
$\text{ReH}_4$	c	-303	e	82

continued over

Results

Table 4.6(x) continued

Molecule	ss	$\Delta H_f^\circ (MX_4)(ss)$	Source	$\Delta H_x(ss)$
$OsCl_4$	g	-79	f	-181
	c	-255	f	-5
$PtCl_4$	c	-263	f	-37
$PtBr_4$	c	-159	f	-18
$SIF_4$	g	-1615	g	-143
$GeF_4$	g	-1190	h	-242
$GeCl_4$	g	-496	g	7
	l	-532	g	43
$SnCl_4$	g	-472	g	-181
	l	-511	g	-142
$PbCl_4$	g	-285	g	-163
	l	-329	g	-119
$TeCl_4$	g	-246	g	-187
	c	-326	g	-107
$TeBr_4$	c	-190	g	-21
$ThCl_4$	c	-1192	i	-34
$UCl_4$	c	-1151	i	-28
$PuCl_4$	c	-921	i	-115

a Wagman et al (1971)

continued over

Results

Table 4.6(x) continued

- b Stull and Prophet(1971)
- c Barnes et al(1974)
- d Rossini et al(1952)
- e Pearcock(1977)
- f Wagman et al(1969)
- g Wagman et al(1968)
- h Gross, Hayman and Ringham(1966)
- i Wagman et al(1972)

Results

associated thermochemical functions are fully discussed in Jenkins and Pratt (1978c). The fact that empirical equations can yield widely inaccurate figures for lattice energies (see Jenkins (1977)) makes it generally difficult to make meaningful comparisons with other work. No work has been presented that approaches the extent of this (no other study deals with more than six salts) and only four use an extended form of calculation for the lattice energy (two of these originating from this laboratory - Jenkins and Smith (1976) and Jenkins (1977); the others being Webster and Collins (1963) and Welsh et al (1974)). The others use the Kapustinskii approach (Efimov and Belorukova (1967), Tsintsis and Smirnova (1969), Hartley (1972), Vdovenko et al (1974a,b) and Lal and Westland (1974)) or the Born-Landé approach (De Jonge (1976)). Lister, Nyburg and Poyntz (1974) use a variety of simple equations for a few salts which is sufficient to show the disparity of results which can be produced and the futility of comparison with extended studies.

The study of hexahalometallate(IV) salts has been a major part of this research. The system has the advantage that there is a wealth of crystal structures available, which yield a lot of related and comparable data. The disadvantages are that some of this data, and also some of

## Results

the thermochemical data used, may be inaccurate due to difficulties in preparing pure compounds; also the crystal structures are predominately cubic (less information is obtained) and charge distributions are difficult to estimate. However although this may not be the best example of the application of the new method because of such problems, the information obtained is extensive and potentially valuable to inorganic chemists, especially in a relative sense.

#### **4.7 The Perchlorate Ion**

The perchlorate ion was chosen to be the first published example of the general application of the new method (Jenkins and Pratt (1978b)) because of the existence of well established, low symmetry, crystal structures of three simple salts (sodium, potassium and ammonium). The results obtained show the new method to its best advantage. They are given in the above reference and not reported further here.

#### **4.8 The Tetrachloroaluminate Ion**

After the success of the calculations on the perchlorate ion (Section 4.8), and motivated by

#### **Results**



correspondence with workers at the University of Lille, it was decided to treat a further tetrahedral ion, the tetrachloroaluminate ion. The crystal structures of salts of this ion had been recently determined with great accuracy, and were found to possess low symmetry hence being ideal for treatment by the newly presented method. The results of earlier studies (Gearhart (1972); Gearhart, Beck and Wood (1975); Jenkins (1976b)) could be checked by the application of this more rigorous method of calculation.

The crystal structures of salts included in this study have all been very recently obtained by the workers at the University of Lille. The crystal structure of the lithium salt is given in Mairesse, Barbier, Wignacourt and Baert (1977). Sodium tetrachloroaluminate had previously been determined by Baenziger (1951) and Scheinert and Weiss (1976). It has recently been refined by Mairesse, Barbier and Wignacourt (1978a). The potassium salt is reported in Mairesse, Barbier and Wignacourt (1978b). The structure for cesium tetrachloroaluminate was determined by Gearhart (1972) and more recently by Mairesse et al (1978a). Ammonium tetrachloroaluminate has been determined (Mairesse, Barbier, Wignacourt, Rubbens and Wallart (1976)) to be isomorphous with the cesium salt and to have

#### Results

freely rotating ammonium ions. The unit cell details of these salts are given in Table 4.8(i).

The program MADELUNG DERIVATIVES (Jenkins and Pratt (1978a)) was run for each structure to obtain the electrostatic energy and cell length derivatives. These terms are calculated as quadratic functions of the charge on the chlorine atoms ( $q_{Cl}$ ), where this is related to the charge on the aluminum atom ( $q_{Al}$ ) by:

$$q_{Al} + 4 q_{Cl} = -1 \quad 4.8(i)$$

They are given, parameterised in the normal fashion, in Table 4.8(ii).

The most suitable dispersion model for the anion is one of four chlorine ions. This should be a reasonable approximation even if the distribution of charge is low. Polarizabilities are taken from Pirene and Kartheuser (1964) and the other parameters used are as usual. The results for the dispersion energies and cell length derivatives are given in Table 4.8(iii).

Comparing this ion to the hexahalometallate ions considered in Section 4.6, and noting the discussion

## Results

Table 4.8(i) Unit cell details for tetrachloroaluminate salts.

Salt	Space group	z	Cell constants (Å)			Angle	M-Cl Dist.
			a	b	c		
$\text{LiAlCl}_4$	$\text{P2}_1/\text{c}$	4	7.007	6.504	12.995	$93.32^\circ$	2.143
$\text{NaAlCl}_4$	$\text{P222}$	4	10.322	9.886	6.167	$90^\circ$	2.136
$\text{KAlCl}_4$	$\text{P2}_1$	4	10.481	7.183	9.273	$93.10^\circ$ *	2.131
$\text{CsAlCl}_4$	$\text{Pnma}$	4	11.641	7.116	9.373	$90^\circ$	2.119
$\text{NH}_4\text{AlCl}_4$	$\text{Pnma}$	4	11.022	7.072	9.257	$90^\circ$	2.117

\* the angle alpha

Results

Table 4.8(ii) Intermediate results for tetrachloro-  
aluminate salts.

Term	$\text{LiAlCl}_4$	$\text{NaAlCl}_4$	$\text{KAlCl}_4$	$\text{CsAlCl}_4$	$\text{NH}_4\text{AlCl}_4$	Units
$A_0$	589.2	556.5	515.5	500.6	510.2	
$U_M$	$A_1$	2599.3	2596.5	2564.7	2609.4	2596.9 $\text{kJ.mol}^{-1}$
	$A_2$	8010.6	8067.0	8007.9	8052.9	8051.9
$U_{SE}$	$B_1$	-2594.9	-2601.4	-2610.9	-2622.5	-2624.4 $\text{kJ.mol}^{-1}$
	$B_2$	-7990.0	-8015.1	-8045.9	-8079.7	-8086.0
$U_{ELEC}$	$C_0$	589.2	556.5	515.5	500.6	510.2
	$C_1$	4.4	-10.8	-46.2	-13.0	-27.4 $\text{kJ.mol}^{-1}$
	$C_2$	20.5	51.9	-38.0	-26.9	-34.1
$\left(\frac{\partial U_{ELEC}}{\partial a}\right)_a$	$D_{a0}$	-47.7	-13.5	-11.4	-12.7	-12.0
	$D_{a1}$	-24.2	-3.8	17.1	6.5	15.1 $\text{kJ.mol}^{-1}$
	$D_{a2}$	-4.5	-13.0	11.3	6.4	9.4 $\text{\AA}^{-1}$
$\left(\frac{\partial U_{ELEC}}{\partial b}\right)_b$	$D_{b0}$	-9.2	-17.6	-34.6	-27.1	-31.1
	$D_{b1}$	7.5	10.8	-17.9	-16.2	-15.8 $\text{kJ.mol}^{-1}$
	$D_{b2}$	-12.7	5.6	15.9	16.2	17.6 $\text{\AA}^{-1}$
$\left(\frac{\partial U_{ELEC}}{\partial c}\right)_c$	$D_{c0}$	-15.0	-39.4	-15.9	-17.0	-17.1
	$D_{c1}$	-11.3	-22.9	4.4	-1.9	-0.3 $\text{kJ.mol}^{-1}$
	$D_{c2}$	-6.6	-35.7	2.4	-0.5	1.4 $\text{\AA}^{-1}$
$U_{dd}$		55.6	60.5	63.6	72.2	69.2 $\text{kJ.mol}^{-1}$

continued over

Results

Table 4.8(ii) continued

Term	$\text{LiAlCl}_4$	$\text{NaAlCl}_4$	$\text{KAlCl}_4$	$\text{CsAlCl}_4$	$\text{NH}_4\text{AlCl}_4$	Units
$\partial u/\partial a$	-20.2	-13.8	-15.6	-15.7	-16.3	
$\partial u/\partial b$	-20.1	-15.5	-22.6	-25.0	-24.9	$\text{kJ.mol}^{-1}$
$\partial u/\partial c$	-11.1	-24.5	-17.1	-19.8	-16.6	$\text{\AA}^{-1}$
$U_{qd}$	4.2	4.7	5.1	6.9	6.0	$\text{kJ.mol}^{-1}$
$\partial U_{qd}/\partial a$	-2.1	-1.4	-1.8	-2.1	-2.0	
$\partial U_{qd}/\partial b$	-2.0	-1.7	-2.5	-3.2	-2.9	$\text{kJ.mol}^{-1}$
$\partial U_{qd}/\partial c$	-1.2	-2.0	-1.9	-1.2	-2.2	$\text{\AA}^{-1}$
$\bar{r}_M$	0.424	0.875	1.191	1.465	1.265	$\text{\AA}$
$U_R^{++}$	0.0	0.0	0.0	0.0	0.0	$\text{kJ.mol}^{-1}$

## Results

regarding repulsion models given there, the only reasonable repulsion model for this anion that can be adopted is one of four spheres centered on the chlorine atoms. The form of the Huggins and Mayer repulsion energy equation is similar to that for the perchlorate ion. Calculations are also performed with a 'spherical anion' model however, in order to estimate a basic radius for the tetrachloroaluminate ion. The cation basic radii are the same as used in other sections where similar ionic polarisabilities are involved, and they are quoted along with the cation-cation repulsion energies in Table 4.8(ii).

Graphs of lattice energy against charge on the chlorine atoms can now be drawn for each salt, and for each different cell length of these salts, using the four sphere model. The curves for lithium tetrachloroaluminate are given in Figure 4.8(i), the order at the left-hand ordinate of the curves resulting from the derivatives with respect to each cell length, from low to high lattice energy, is b-c-a. Figure 4.8(ii) shows the curves for the sodium salt (order a-c-b), Figure 4.8(iii) for the potassium salt (order c-a-b) and Figure 4.8(iv) for the cesium salt (order a-c-b). The curves for ammonium tetrachloroaluminate are not shown as they are virtually

#### Results

Figure 4.8(1) Lattice energy of lithium tetrachloroaluminate.

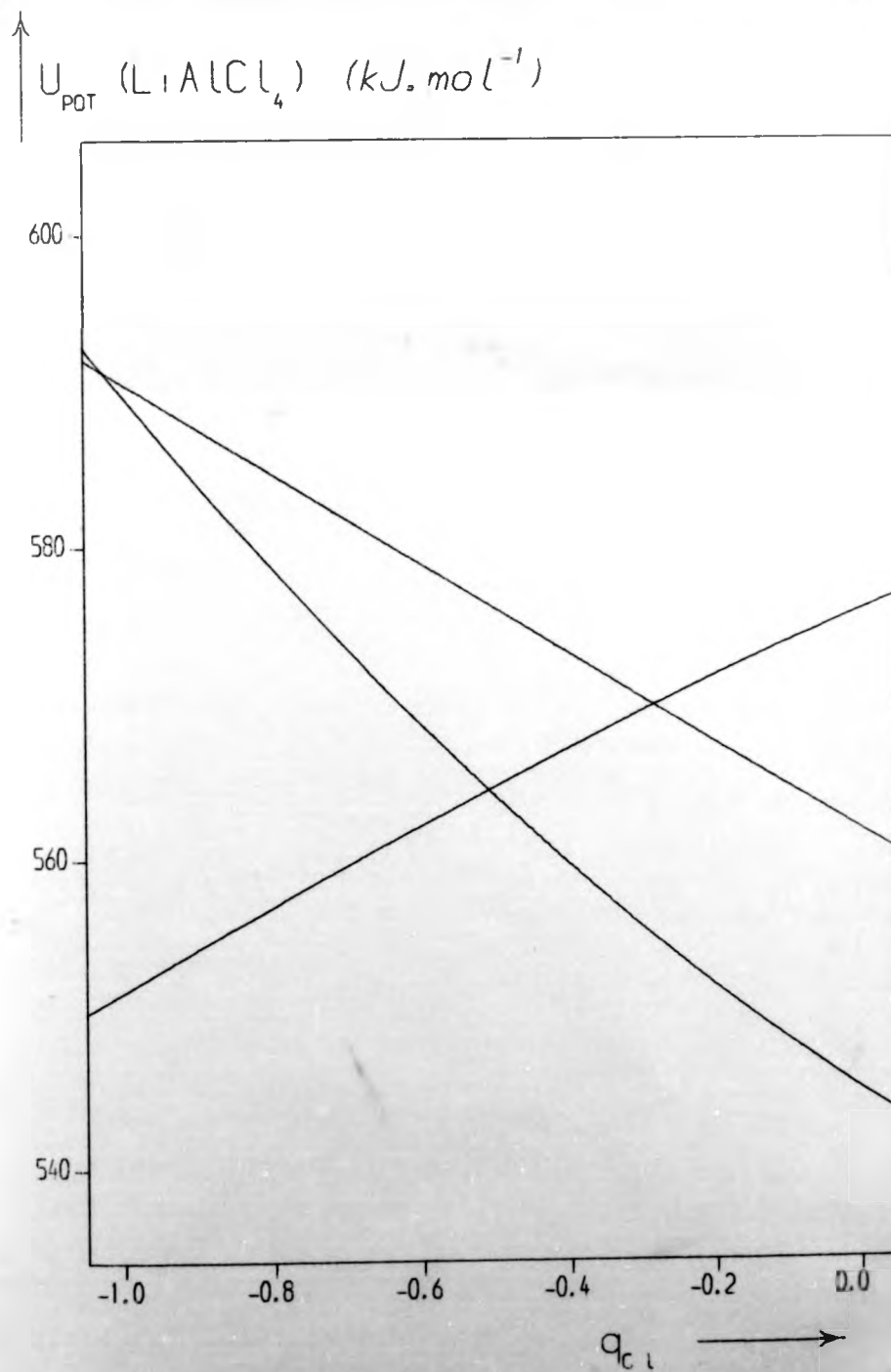


Figure 4.8(ii) Lattice energy of sodium tetrachloroaluminate.

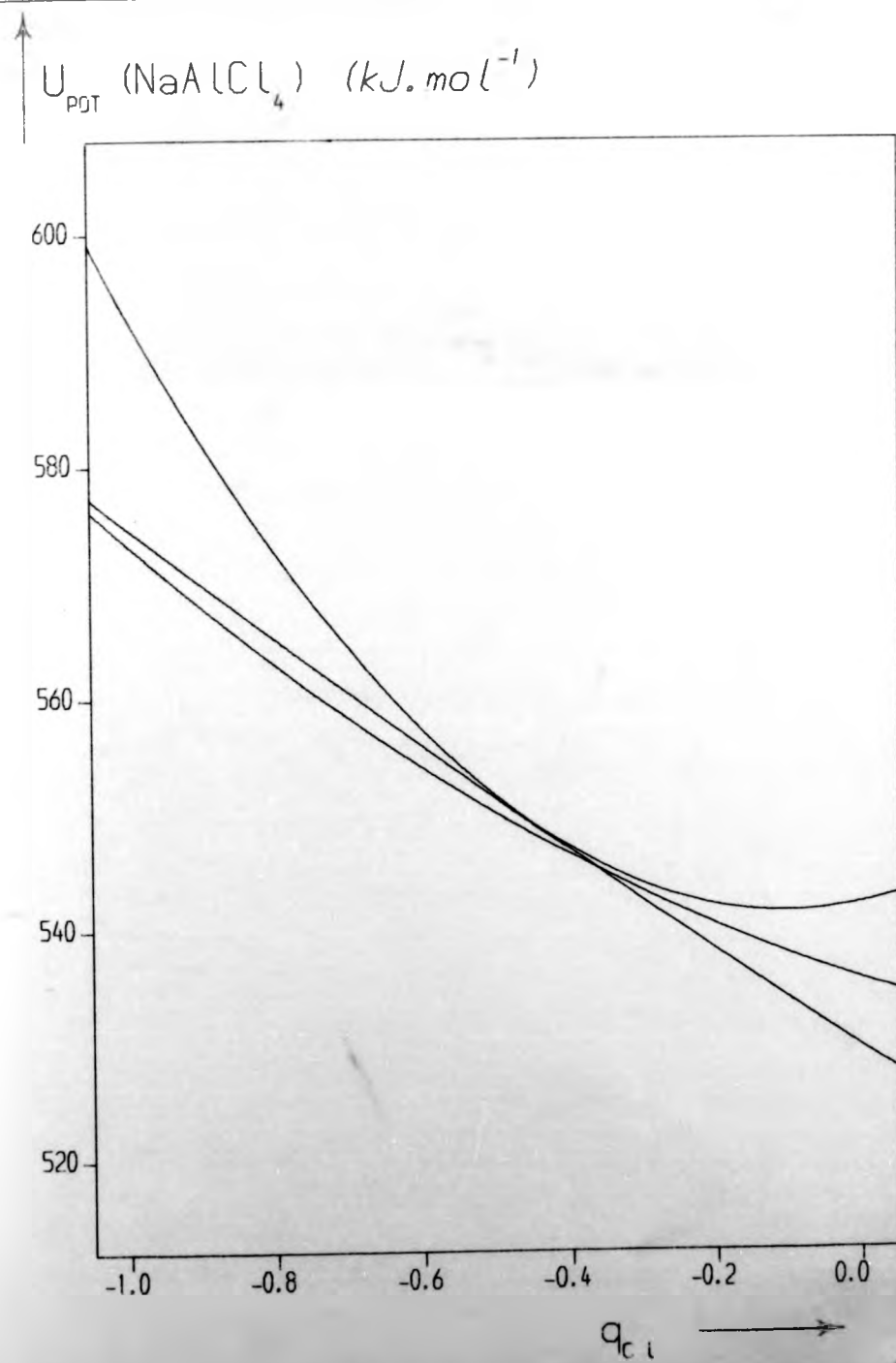




Figure 4.8(iii) Lattice energy of potassium tetrachloroaluminate.

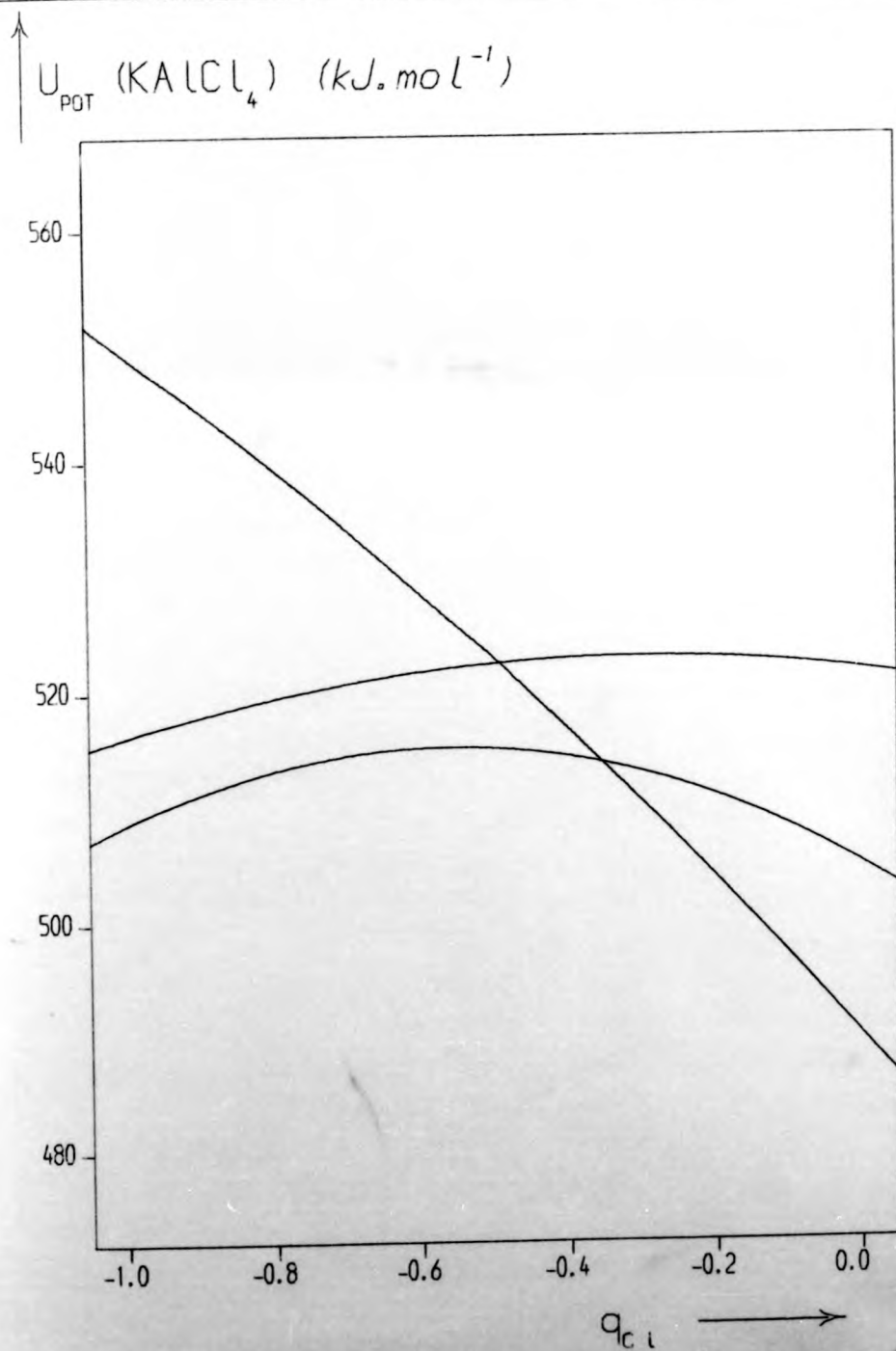
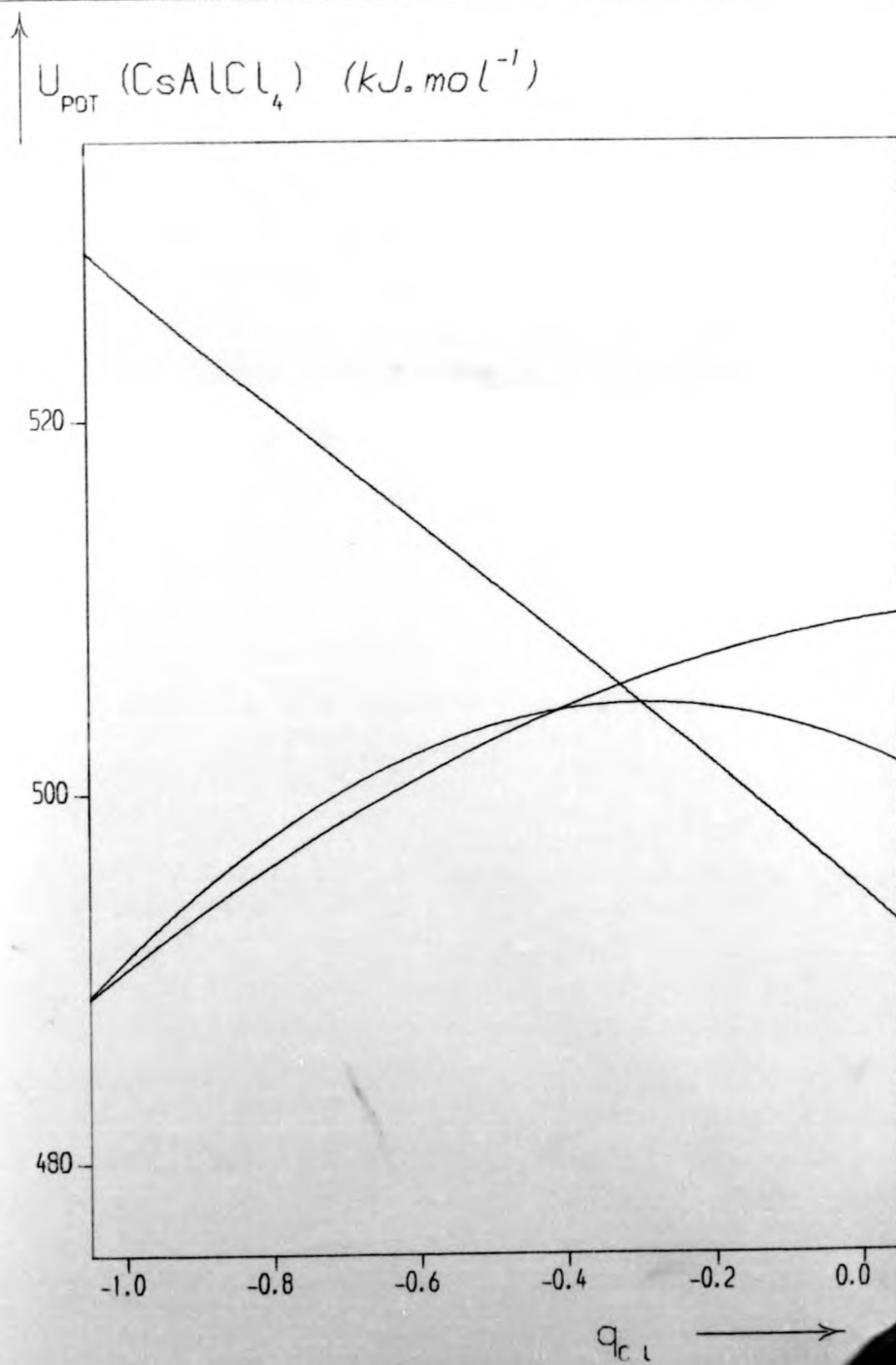


Figure 4.8(iv) Lattice energy of cesium tetrachloroaluminate.



identical to those for the cesium salt.

Assignment of values can now proceed from the intersection points of these curves. Due to the similarities between the shapes of some curves not all intersections are included in the assignment. Those that are considered to give most accurate results are listed in Table 4.3(iii). From this table we can assign:

$$q_{Cl} = -0.38 \pm 0.07 \quad 4.8(ii)$$

$$\bar{r}_{Cl} = 1.36 \pm 0.01 \text{ \AA} \quad 4.8(iii)$$

$$U_{POT}(LiAlCl_4) = 567 \text{ kJ.mol}^{-1} \quad 4.8(iv)$$

$$U_{POT}(NaAlCl_4) = 545 \text{ kJ.mol}^{-1} \quad 4.8(v)$$

$$U_{POT}(KAlCl_4) = 518 \text{ kJ.mol}^{-1} \quad 4.8(vi)$$

$$U_{POT}(CsAlCl_4) = 505 \text{ kJ.mol}^{-1} \quad 4.8(vii)$$

and

$$U_{POT}(NH_4AlCl_4) = 522 \text{ kJ.mol}^{-1} \quad 4.8(viii)$$

The thermochemical cycle that relates the lattice enthalpy to the enthalpy of formation of the gaseous tetrachloroaluminate ion gives the equality:

$$\Delta H_F^\circ(AlCl_4^-)(g) = U_{POT}(MAlCl_4) + \Delta H_F^\circ(MAlCl_4) - \Delta H_F^\circ(M^+)(g) + \frac{1}{2}RT \quad 4.8(ix)$$

#### Results

Table 4.8(iii) Intersection points to be used for assignment of values for tetrachloroaluminate salts.

Salt	Intersection	$q_{Cl}$	$\bar{r}_{Cl}(\text{\AA})$	$U_{POT}(\text{kJ.mol}^{-1})$
$LiAlCl_4$	ab	-0.51	1.361	564.4
	bc	-0.29	1.329	565.8
$NaAlCl_4^*$	ac	-0.36	1.353	545.2
$KAlCl_4$	ab	-0.49	1.334	522.5
	bc	-0.35	1.351	513.9
$CsAlCl_4$	ab	-0.33	1.361	505.7
	ac	-0.41	1.367	504.4
	bc	-0.30	1.363	504.8
$NH_4AlCl_4$	ab	-0.37	1.366	523.1
	ac	-0.44	1.373	522.1
	bc	-0.33	1.369	521.8

\* in Figure 4.8(ii) the b and c curves appear to touch although they don't actually meet.

#### Results

The enthalpies of formation of the lithium and ammonium salts are unfortunately undetermined, but using the data in Table 4.8(iv) for the other salts we can plot the curves in Figure 4.8(v) (order at the left-hand ordinate:  $K_o$ ,  $K_a$ ,  $Cs_a$ ,  $Cs_o$ ,  $Na_a$ ,  $Na_o$ ,  $K_b$ ,  $Na_b$ ,  $Cs_b$ ). The results from the cesium salt are again found to be slightly at variance with the others although they are included in making the assignment:

$$\Delta H_f^\circ(AlCl_4^-)(g) = -1187 \pm 18 \text{ kJ.mol}^{-1} \quad 4.8(x)$$

where the error quoted is the standard deviation of the average. The questionable results for cesium salts obtained throughout this study means the true value is likely to be on the negative side of the above.

Using a cycle similar to that used in Section 4.6 the chloride ion affinity of aluminum chloride in its standard state(s) ( $\Delta H_{Cl(ss)}^\circ$ ) may be obtained by:

$$\Delta H_{Cl(ss)}^\circ = \Delta H_f^\circ(AlCl_4^-)(g) - \Delta H_f^\circ(AlCl_3)(ss) - \Delta H_f^\circ(Cl^-)(g) \quad 4.8(xi)$$

Using the data in Table 4.8(iv) enables the

## Results

Figure 4.8(v) Enthalpy of formation of the gaseous tetrachloroaluminate ion.

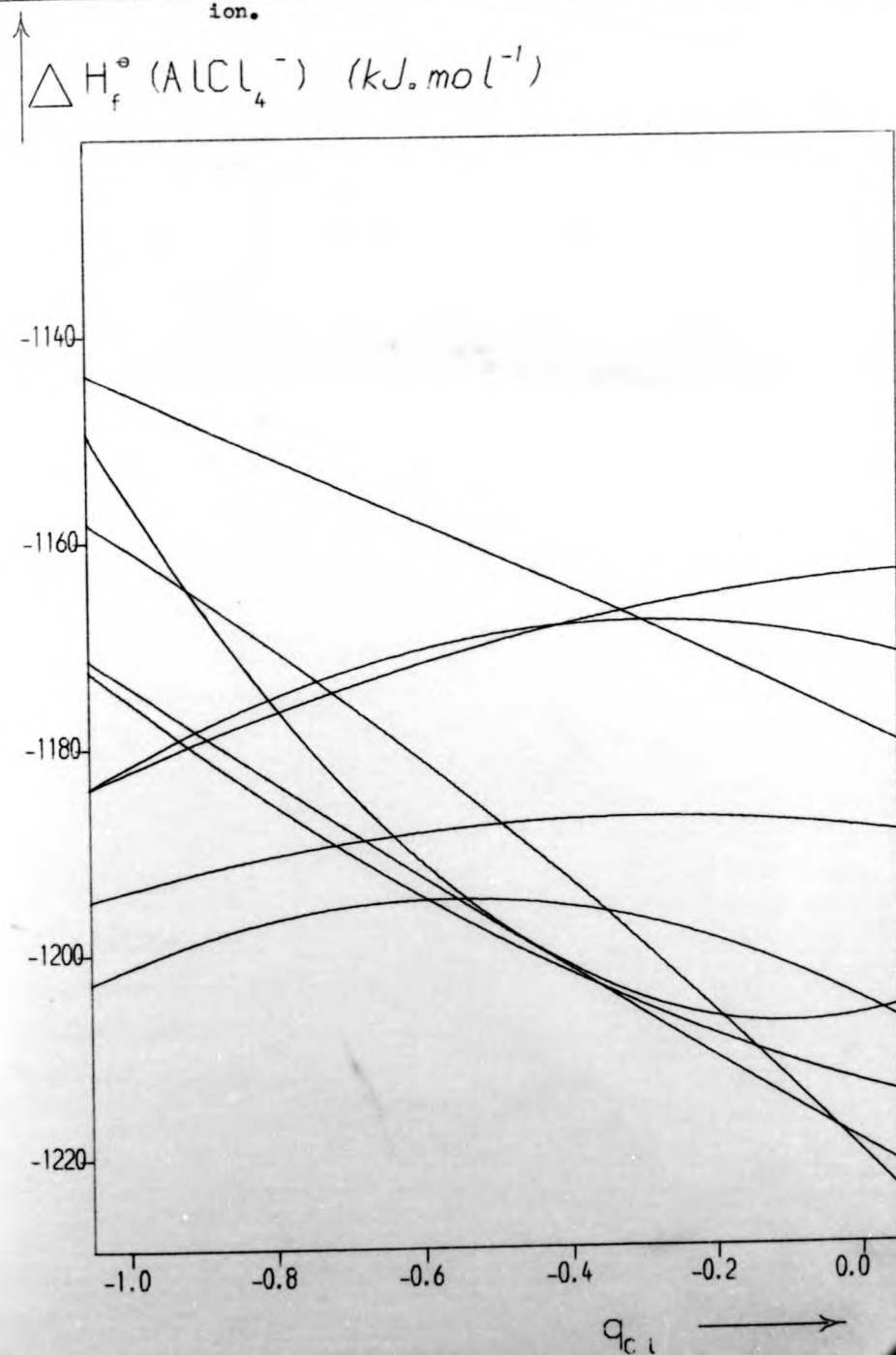


Table 4.6(iv) Ancillary thermochemical data for use with the tetrachloroaluminate ion calculations ( $\text{kJ.mol}^{-1}$ ).

X	$\Delta_f H^\circ(X)(ss)$	ss	Ref.
$\text{NaAlCl}_4$	-1140*	c	a
$\text{KAlCl}_4$	-1197	c	b
$\text{CsAlCl}_4$	-1222	c	a
$\text{Na}^+$	609.8	g	b
$\text{K}^+$	514.2	g	b
$\text{Cs}^+$	452.3	g	b
$\text{AlCl}_3$	-585	g	b
$\text{AlCl}_3$	-675	l	b
$\text{AlCl}_3$	-706	c	b
$\text{Cl}^-$	-246	g	c

\* in good agreement with the value in b

a Gearhart, Beck and Wood (1975)

b Stull and Prophet (1971)

c Cox et al (1972)

## Results

assignments:

$$\Delta H_{\text{Cl}(g)}^{\circ} = -356 \text{ kJ.mol}^{-1} \quad 4.8(\text{xi})$$

$$\Delta H_{\text{Cl}(l)}^{\circ} = -266 \text{ kJ.mol}^{-1} \quad 4.8(\text{xii})$$

$$\Delta H_{\text{Cl}(o)}^{\circ} = -235 \text{ kJ.mol}^{-1} \quad 4.8(\text{xiv})$$

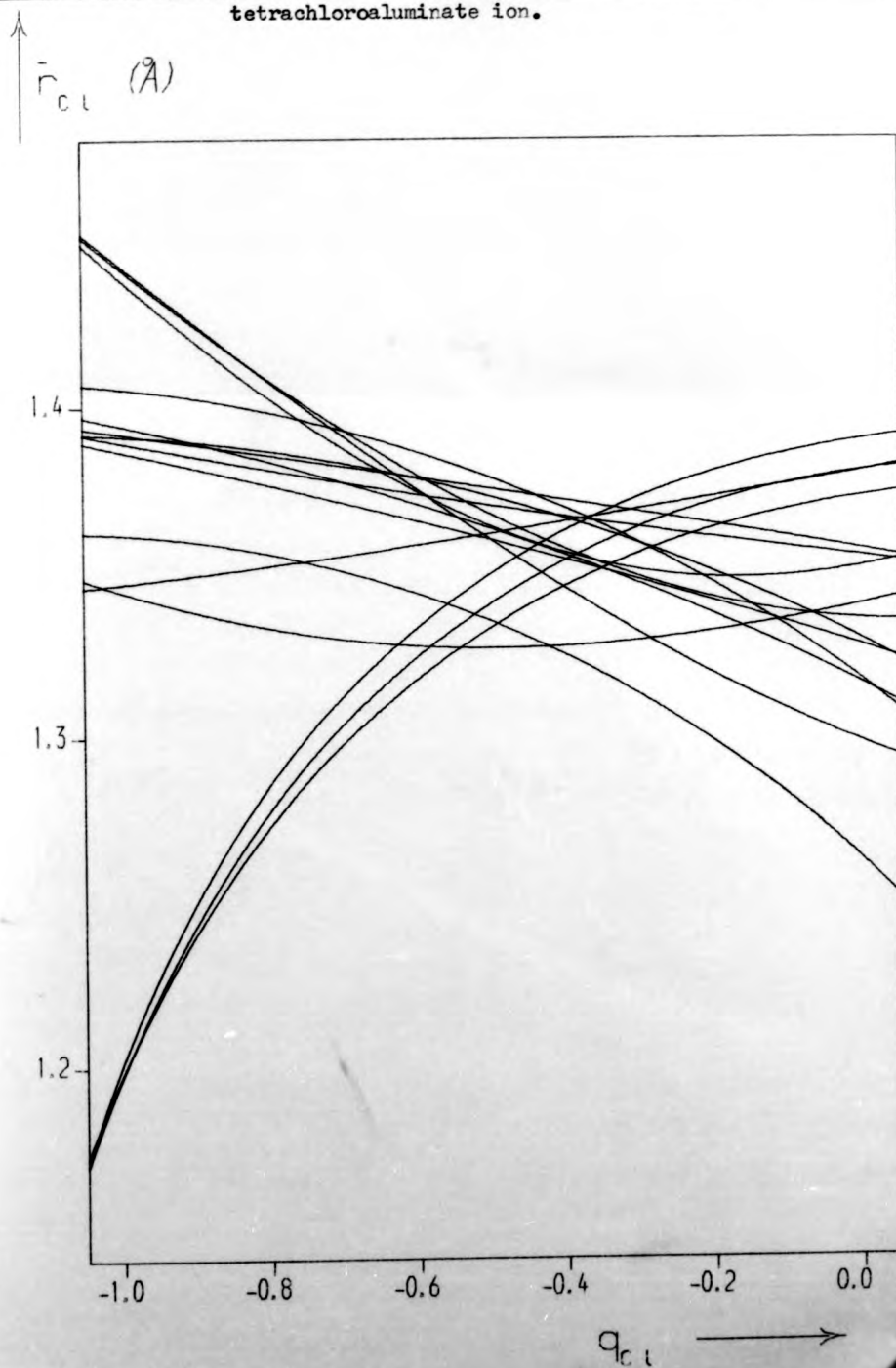
From calculations using the 'spherical anion' repulsion model for the tetrachloroaluminate ion it is possible to estimate the basic radius of the ion to be  $2.45 \pm 0.1 \text{ \AA}$ , although this can at best only be a very approximate value. However the basic radius of the chlorine atom ( $r_{\text{Cl}}$ ) from the 'four sphere' model may be treated as an ion property and plotted against the charge on the chlorine atom. This is done in Figure 4.8(vi), from which the assignment in Equation 4.8(iii) is made. This quantity is surprisingly constant over the five salts which shows that the forces present in the crystals must be similar.

Previous workers (Gearhart, Beck and Wood (1975) and Jenkins (1976b)) have performed calculations on the cesium and sodium salts using forms of the Jenkins and Waddington equation. The results they obtained for the enthalpy of formation of the gaseous anion and the chloride ion

## Results



Figure 4.8(vi) Basic radius of the chlorine atoms of the tetrachloroaluminate ion.



affinity of aluminum chloride agree well with the values assigned here. However the lattice energy results do disagree by a small amount, in one case (Jenkins (1976)) this is mainly due to the assignment of a greater charge distribution ( $q_{Cl} = -0.59$ ).

These calculations on the tetrachloroaluminate ion again show the internal consistency of the results that can be produced by the application of the newly proposed method. The unsatisfactory state of the knowledge concerning the enthalpies of formation of the crystalline salts, due to their hygroscopic nature, is the one thorn in the side of an otherwise very successful study.

#### 4.9 The Peroxide Ion

The peroxide ion is a complex ion with a known charge distribution, due to symmetry each oxygen atom must have a nett charge of -1. This removes one of the two major unknowns from the lattice energy equation, leaving only the basic radius (radii) assigned to the peroxide ion.

Metal peroxides have been the subject of lattice energy studies by Pavlyuchenko and Popova (1963a,b) and Wood and D'Grazio (1965). The former workers used the

#### Results

Kapustinskii equation whilst the latter Wood's adaptation of the Ladd and Lee equation. Both sets of results show wide variation in the values for the enthalpy of formation of the gaseous peroxide ion (the values, with standard deviation, from the two studies are, for the former,  $468 \pm 81$  and, for the latter,  $607 \pm 63$  kJ.mol<sup>-1</sup>). It was hoped that by application of the new method that a more consistent result could be obtained and the large difference between the two studies investigated.

The crystal structures of the alkali metal, calcium, strontium and barium salts are taken from Wyckoff. The structure for magnesium peroxide is taken from Vannerberg (1959). The unit cell details are given in Table 4.9(i).

The program MODELING DERIVATIVES (Jenkins and Pratt (1978a)) was run to give the values for the electrostatic energy and cell length derivatives quoted in Tables 4.9(ii) and 4.9(iii).

Kazarnovskii and Raikhshein (1947) quote the polarisability of O<sup>-</sup> as  $2.12 \times 10^{-30}$  m<sup>3</sup>. They use cation polarisabilities from Pauling (1927) and consequently they are also employed in this work. The characteristic energy of the oxygen negative ion is estimated from the electron

## Results

Table 4.9(i) Unit cell details for metal peroxides.

Salt	Space group	z	Cell constants (Å)			O-O dist.
			a	b	c	
$\text{Li}_2\text{C}_2$	$\text{P}\bar{6}$	2	3.142	(=a)	7.650	1.51
$\text{Na}_2\text{C}_2$	$\text{C62m}$	3	6.208	(=a)	4.460	1.495
$\text{K}_2\text{O}_2$	$\text{Cmca}$	4	6.736	7.001	6.479	1.50
$\text{Rb}_2\text{C}_2$	$\text{Immm}$	2	4.261	7.075	5.983	1.50
$\text{Cs}_2\text{O}_2$	$\text{Immm}$	2	4.322	7.517	6.430	1.50
$\text{MgO}_2$	$\text{Pa}\bar{3}$	4	4.839	(=a)	(=a)	1.49
$\text{CaO}_2$	$\text{I4/mmm}$	2	3.54	(=a)	5.92	1.50
$\text{SrO}_2$	$\text{I4/mmm}$	2	3.567	(=a)	6.6161	1.50
$\text{BaO}_2$	$\text{I4/mmm}$	2	3.8154	(=a)	6.6513	1.49

Results

Table 4.9(ii) Intermediate results for alkali metal peroxides.

Term	Li <sub>2</sub> O <sub>2</sub>	Na <sub>2</sub> O <sub>2</sub>	K <sub>2</sub> O <sub>2</sub>	Rb <sub>2</sub> O <sub>2</sub>	Cs <sub>2</sub> O <sub>2</sub>	Units
$U_M$	2175.7	1752.5	1471.9	1345.8	1235.4	kJ.mol <sup>-1</sup>
$U_{SE}$	917.2	527.1	926.3	928.8	923.4	
$U_{ELEC}$	3092.9	2679.6	2398.2	2274.7	2158.8	kJ.mol <sup>-1</sup>
$(\partial U_{ELEC} / \partial a)_{a=a_0}^d$	-725.4	-319.5	-132.4	-166.1	-150.1	
$(\partial U_{ELEC} / \partial b)_{b=b_0}^d$	-	-	-95.4	-120.9	-113.8	kJ.mol <sup>-1</sup>
$(\partial U_{ELEC} / \partial c)_{c=c_0}^d$	-69.3	-124.3	-111.2	-108.6	-90.3	Å <sup>-1</sup>
$U_{dd}$	99.3	81.5	59.3	116.2	147.9	kJ.mol <sup>-1</sup>
$\partial U_{dd} / \partial a$	-139.7	-56.3	-32.7	-58.7	-74.7	
$\partial U_{dd} / \partial b$	-	-	-29.9	-36.1	-43.7	kJ.mol <sup>-1</sup>
$\partial U_{dd} / \partial c$	-22.6	-35.7	-30.5	-34.3	-37.1	Å <sup>-1</sup>
$U_{qd}$	14.9	8.3	11.2	14.5	20.7	kJ.mol <sup>-1</sup>
$\partial U_{qd} / \partial a$	-21.4	-7.7	-5.0	-9.8	-14.6	
$\partial U_{qd} / \partial b$	-	-	-3.9	-6.2	-8.5	kJ.mol <sup>-1</sup>
$\partial U_{qd} / \partial c$	-3.1	-4.8	-4.6	-5.5	-6.0	Å <sup>-1</sup>
$\bar{r}_M$	0.456	0.875	1.190	1.320	1.467	Å
$U_R^{++}$	6.1	13.5	22.9	29.3	36.8	kJ.mol <sup>-1</sup>

Results

Table 4.9(iii) Intermediate results for alkaline earth peroxides.

Term	MgO <sub>2</sub>	CaO <sub>2</sub>	SrO <sub>2</sub>	BeO <sub>2</sub>	Units
$U_M$	3071.8	2667.5	2540.2	2354.6	$\text{kJ.mol}^{-1}$
$U_{SE}$	931.2	926.1	925.9	931.0	
$U_{ELEC}$	4003.0	3613.6	3466.1	3285.7	$\text{kJ.mol}^{-1}$
$(\partial U_{ELEC} / \partial a)_{a=a_0}^d$	-818.2	-571.9	-637.8	-569.6	$\text{kJ.mol}^{-1}$
$(\partial U_{ELEC} / \partial c)_{c=c_0}^d$	-	-249.1	-138.5	-132.5	$\text{\AA}^{-1}$
$U_{dd}$	134.6	133.1	140.5	146.7	$\text{kJ.mol}^{-1}$
$\partial U_{dd} / \partial a$	-179.9	-142.6	-165.6	-162.1	$\text{kJ.mol}^{-1}$
$\partial U_{dd} / \partial c$	-	-62.2	-42.6	-43.6	$\text{\AA}^{-1}$
$U_{qd}$	15.3	16.5	18.8	23.0	$\text{kJ.mol}^{-1}$
$\partial U_{qd} / \partial a$	-27.9	-21.2	-29.5	-33.0	$\text{kJ.mol}^{-1}$
$\partial U_{qd} / \partial c$	-	-12.6	-7.6	-9.2	$\text{\AA}^{-1}$
$\bar{r}_M$	0.748	1.142	1.266	1.424	$\text{\AA}$
$U_R^{++}$	2.1	8.4	12.4	15.6	$\text{kJ.mol}^{-1}$

Results

affinity of the oxygen radical. The dispersion energies and cell length derivatives are given in Tables 4.9(ii) and 4.9(iii).

The cation basic radii are taken from Section 4.2 and they are quoted with the cation-cation repulsion energies in the same tables.

A repulsion model for the anion of two spheres centered on the oxygen atoms is the only viable possibility. It was hoped that similar problems to those present in the cyanide ion calculations were not applicable here. Using this model each derivative of each salt defines a value for the basic radii of these spheres, hence a lattice energy and hence the enthalpy of formation of the gaseous peroxide ion, by the thermochemical cycle where:

$$\Delta H_f^\circ(O_2^{2-})(g) = U_{POT}(M_mO_2) + \Delta H_f^\circ(M_mO_2)(c) - m\Delta H_f^\circ(M^{(3-m)+})(g) + nRT \quad 4.9(i)$$

$n=0$  for  $m=1$  (divalent  $M$ ) and  $n=1/2$  for  $m=2$  (monovalent  $M$ ). The values of all these parameters, for each derivative of each salt, are given in Table 4.9(iv). The results in the final column use the thermochemical

Table 4.9(iv) Final results for metal peroxides  
( $\text{kJ}\cdot\text{mol}^{-1}$ ).

Salt	Derivative	$\bar{r}_0(\text{\AA})$	$U_{\text{POT}}$	$\Delta H_f^\circ(\text{O}_2^{2-})(\text{g})$
$\text{Li}_2\text{O}_2$	a	1.230	2661.8	651.5
	c	1.342	2408.1	397.8
$\text{Na}_2\text{O}_2$	a	1.248	2329.4	603.9
	c	1.236	2344.7	619.2
$\text{K}_2\text{O}_2$	a	1.253	2136.1	614.8
	b	1.240	2150.9	627.6
	c	1.242	2149.0	625.6
$\text{Rb}_2\text{O}_2$	a	1.220	2076.6	660.1
	b	1.249	2050.1	633.6
	c	1.263	2076.5	620.0
$\text{Cs}_2\text{O}_2$	a	1.193	2018.6	697.6
	b	1.249	1970.2	649.2
	c	1.297	1922.2	601.3
$\text{H}_2\text{O}_2$	a	1.306	1513.5	542.0
$\text{CaO}_2$	a	1.250	3155.7	577.1
	c	1.189	3263.6	685.0
$\text{SrO}_2$	a	1.229	3090.3	666.2
	c	1.214	3114.5	690.4
$\text{BaO}_2$	a	1.220	2949.6	654.9
	c	1.195	2985.2	690.4

Results



data given in Table 4.9(v).

From the results in Table 4.9(iv) it is possible to make the assignments below, where the quoted errors are the standard deviation of the averages. The results from the a derivative are doubly weighted for hexagonal and tetragonal structures and triply weighted for cubic structures.

$$\bar{r}_0 = 1.25 \pm 0.04 \text{ \AA} \quad 4.9(ii)$$

$$U_{\text{POT}}(\text{Li}_2\text{O}_2) = 2577 \text{ kJ.mol}^{-1} \quad 4.9(iii)$$

$$U_{\text{POT}}(\text{Na}_2\text{O}_2) = 2335 \text{ kJ.mol}^{-1} \quad 4.9(iv)$$

$$U_{\text{POT}}(\text{K}_2\text{O}_2) = 2146 \text{ kJ.mol}^{-1} \quad 4.9(v)$$

$$U_{\text{POT}}(\text{Rb}_2\text{O}_2) = 2054 \text{ kJ.mol}^{-1} \quad 4.9(vi)$$

$$U_{\text{POT}}(\text{Cs}_2\text{O}_2) = 1970 \text{ kJ.mol}^{-1} \quad 4.9(vii)$$

$$U_{\text{POT}}(\text{MgO}_2) = 3514 \text{ kJ.mol}^{-1} \quad 4.9(viii)$$

$$U_{\text{POT}}(\text{CaO}_2) = 3192 \text{ kJ.mol}^{-1} \quad 4.9(ix)$$

$$U_{\text{POT}}(\text{SrO}_2) = 3098 \text{ kJ.mol}^{-1} \quad 4.9(x)$$

$$U_{\text{POT}}(\text{BaO}_2) = 2961 \text{ kJ.mol}^{-1} \quad 4.9(xi)$$

and

$$\Delta H_f^\circ(\text{O}_2^{2-})(g) = 620 \pm 63 \text{ kJ.mol}^{-1} \quad 4.9(xii)$$

## Results

data given in Table 4.9(v).

From the results in Table 4.9(iv) it is possible to make the assignments below, where the quoted errors are the standard deviation of the averages. The results from the a derivative are doubly weighted for hexagonal and tetragonal structures and triply weighted for cubic structures.

$$\bar{r}_0 = 1.25 \pm 0.04 \text{ \AA} \quad 4.9(ii)$$

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$$U_{\text{POT}}(\text{Na}_2\text{O}_2) = 2335 \text{ kJ.mol}^{-1} \quad 4.9(iv)$$

$$U_{\text{POT}}(\text{K}_2\text{O}_2) = 2146 \text{ kJ.mol}^{-1} \quad 4.9(v)$$

$$U_{\text{POT}}(\text{Rb}_2\text{O}_2) = 2054 \text{ kJ.mol}^{-1} \quad 4.9(vi)$$

$$U_{\text{POT}}(\text{Cs}_2\text{O}_2) = 1970 \text{ kJ.mol}^{-1} \quad 4.9(vii)$$

$$U_{\text{POT}}(\text{MgO}_2) = 3514 \text{ kJ.mol}^{-1} \quad 4.9(viii)$$

$$U_{\text{POT}}(\text{CaO}_2) = 3192 \text{ kJ.mol}^{-1} \quad 4.9(ix)$$

$$U_{\text{POT}}(\text{SrO}_2) = 3098 \text{ kJ.mol}^{-1} \quad 4.9(x)$$

$$U_{\text{POT}}(\text{BaO}_2) = 2961 \text{ kJ.mol}^{-1} \quad 4.9(xi)$$

and

$$\Delta H_f^\circ(\text{O}_2^{2-})(g) = 620 \pm 63 \text{ kJ.mol}^{-1} \quad 4.9(xii)$$

## Results

Table 4.9(v) Thermochemical data for peroxide salts  
(kJ.mol<sup>-1</sup>).

Salt	$\Delta_f^\circ(\text{salt})(\text{c})$	$\Delta_f^\circ(\text{M}^+ \text{ or } \text{M}^{2+})(\text{g})$
Li <sub>2</sub> O <sub>2</sub>	-151.2a	687.2a
Na <sub>2</sub> O <sub>2</sub>	-122.7a	609.2a
K <sub>2</sub> O <sub>2</sub>	-119. b	514.2a
Rb <sub>2</sub> O <sub>2</sub>	-101.7b	494.9b
Cs <sub>2</sub> O <sub>2</sub>	-96.2b	452.3a
H <sub>2</sub> O <sub>2</sub>	-149.9b	2348.5c
CaO <sub>2</sub>	-156.0c	1925.9c
SrO <sub>2</sub>	-151.4c	1790.6c
BaO <sub>2</sub>	-151.6c	1660.5c

a Stull and Prophet(1971)

b Fossini et al(1952)

c Wagman et al(1971)

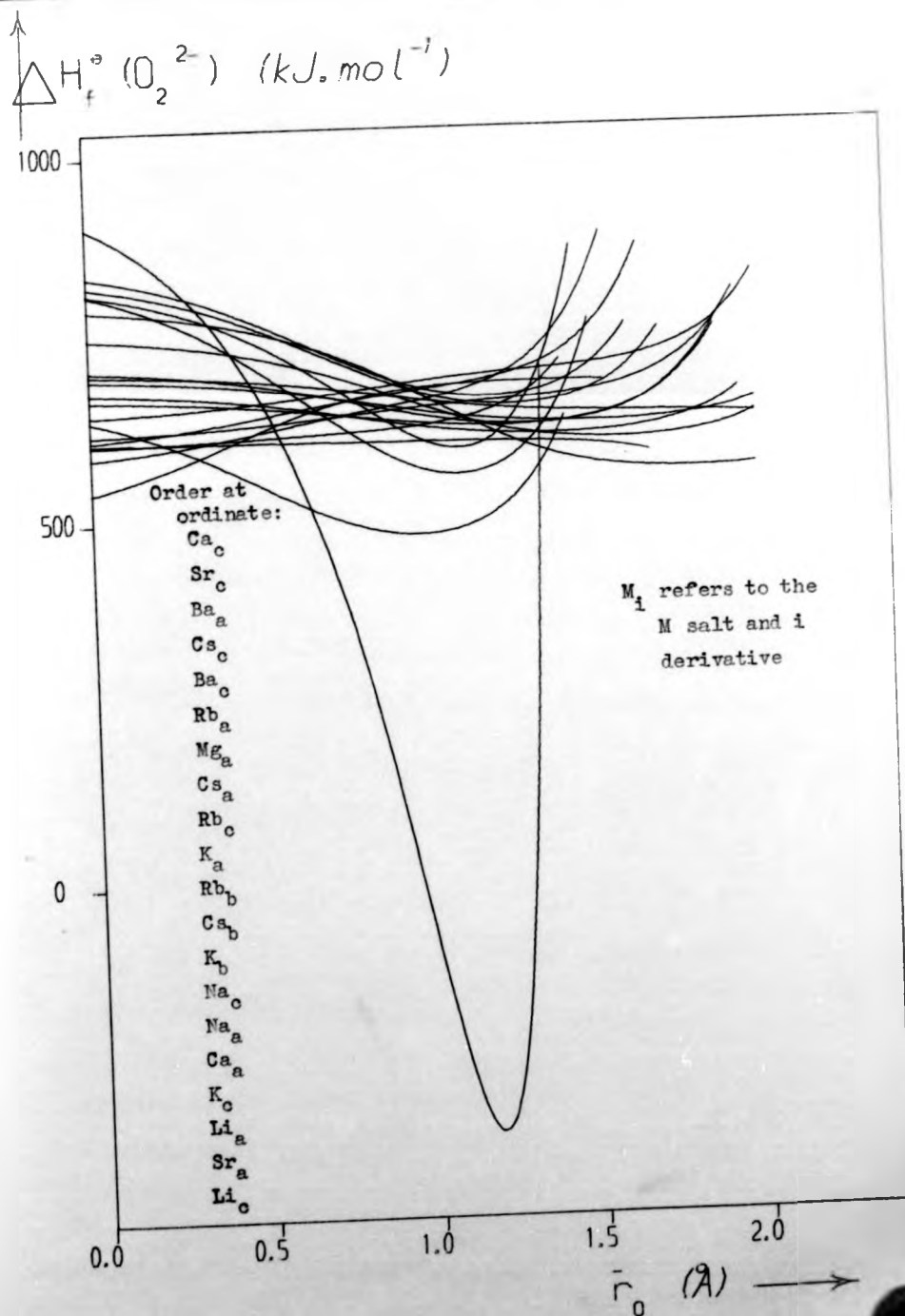
## Results

A graphical representation of these results is given in Figure 4.9(i) where the enthalpy of formation of the gaseous peroxide ion is plotted against the 'unknown' basic radius for all the different derivatives of all the salts. The lack of a unique, or even remotely unique, intersection point in the figure and the corresponding spread of the results is obviously disappointing. Despite the large amount of data produced the spread is the same as found by Wood and D'Craio (1965) as is the region of the mean value. This basic agreement, despite some quite large disagreements over individual lattice energies, means that the value produced for the enthalpy of formation of the anion should at least be accurate to the range quoted.

The results obtained, being quite varied, would seem at first sight a condemnation of the present method. However as similar ranges have been produced by the previous workers it would appear certain that the disparity is a property of the system, something which the method could not overcome. Several workers have separately determined the thermochemical data so it seems that this should be accurate if no impurities, in the form of other oxygen oxidation states, are assumed present in the samples used. Covalency and polarisation forces will

#### Results

Figure 4.9(i) Enthalpy of formation of the gaseous peroxide ion.



probably play a large part in the alkaline earth metal salts, this could explain some of the uncertainty but by no means all. It seems that, unless the crystal structures are greatly at fault, some other forces are present in these salts which have not been taken into account by the method.

#### 4.10 The Hexafluorotungstate(V) Ion

As a result of collaboration with workers from the University of Leicester over some aspects of the study on hexahalometallate(IV) ions it was decided to carry out some preliminary investigations regarding the hexafluorotungstate(V) ion, a subject in which they have been interested for some time (Burgess, Haigh and Peacock (1971); Burgess et al (1974); Burgess and Peacock (1977)). The newly proposed method can be used to investigate some tentative data for the crystal structures of alkali metal salts.

The crystal structures for lithium, sodium, potassium and cesium hexafluorotungstate have been tentatively assigned by Peacock (1978). He proposed sets of atomic coordinates to be allied with experimental unit cell dimensions. For the sodium salt he proposed two sets of

#### Results

coordinates for ordered structures, here designated A and B. The uncertainties with all these structures is due to the difficulties of growing single crystals, and those associated with the analysis of poor reflection data. The unit cell details proposed are given in Table 4.10(i).

The calculations on these salts were carried out using the program LATEN described in Section 3. The electrostatic terms were computed as quadratic functions of the charge on the fluorine atoms ( $q_F$ ). This is related to the net charge on the tungsten atom ( $q_W$ ) by:

$$q_W + 6 q_F = -1 \quad 4.10(i)$$

A dispersion model of six fluorine ions is taken and the polarisabilities of Pirene and Kartheiser (1964) used. All intermediate results are given in Table 4.10(ii), parameterised in the usual fashion.

In accord with the calculations on the similar doubly charged anions a repulsion model of six spheres at the fluorine positions is chosen. The calculation for the lattice energy can now be completed. The lattice energy of lithium hexafluorotungstate is plotted against the charge on the fluorine atoms in Figure 4.10(i) (the curve

#### Results

Figure 4.10(i) Lattice energy of lithium hexafluorotungstate.

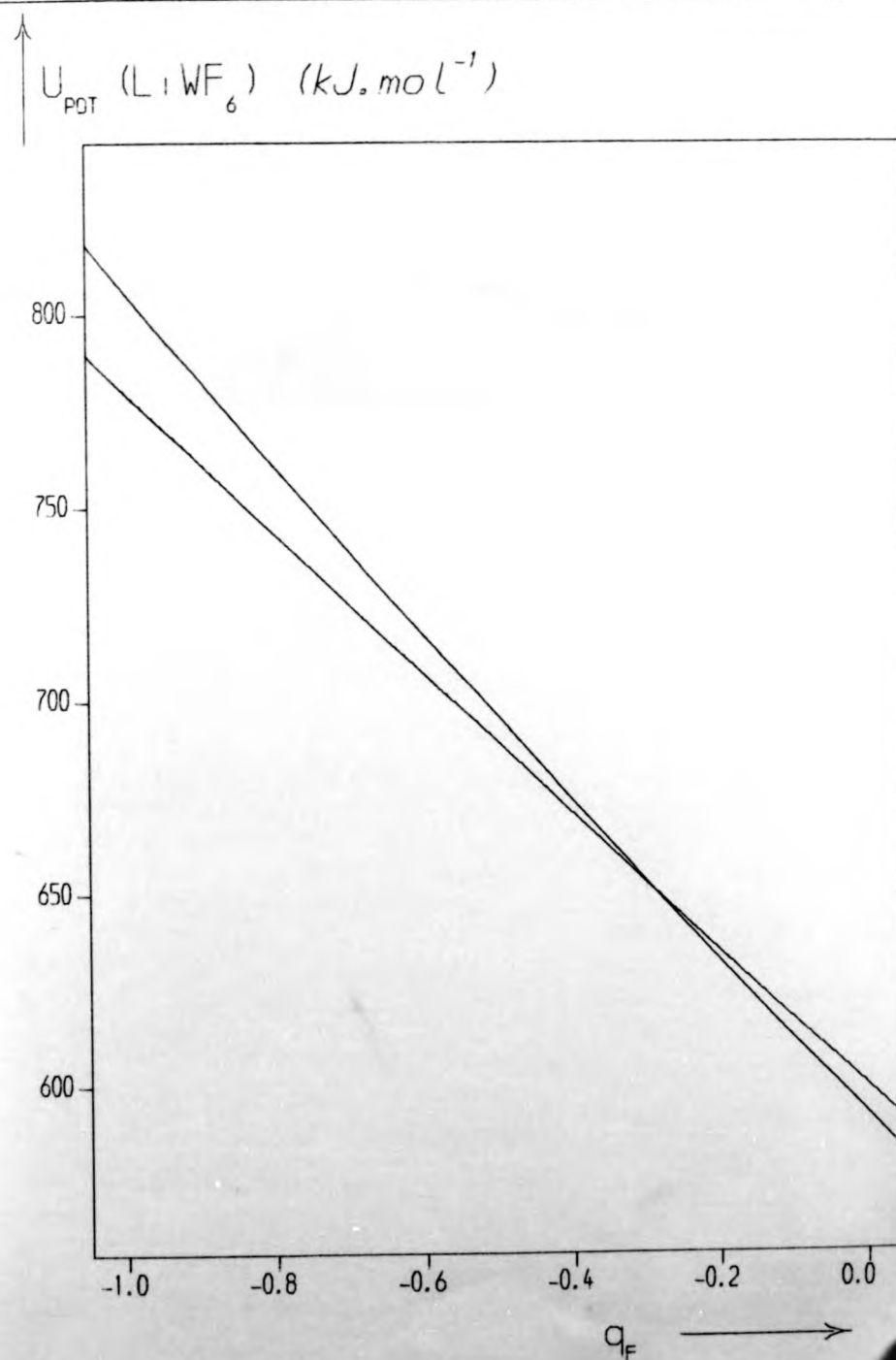




Table 4.10(i) Proposed unit cell details for  
hexafluorotungstate(V) salts.

Salt	Space group	z	Cell constants ( $\text{\AA}$ )			W-F dist.
			a	c	$\alpha$	
$\text{LiWF}_6$	$R\bar{3}$	3	5.234	13.61	$90^\circ$	1.892
$\text{NaWF}_6$	$\text{Pa}\bar{3}$	4	9.18	(=a)	$90^\circ$	1.877*
$\text{KWF}_6$	$\text{P}\bar{4}2_1$	2	5.105	10.09	$90^\circ$	1.830
$\text{CsWF}_6$	$R\bar{3}\text{m}$	1	5.31	(=a)	$95.3^\circ$	1.833

\* identical for the alternative sets of fluorine  
coordinates

## Results

Table 4.10(ii) Intermediate results for hexafluorotungstate(V) salts.

Term	LiWF <sub>6</sub>	NaWF <sub>6</sub> (A)	NaWF <sub>6</sub> (B)	KWF <sub>6</sub>	CsWF <sub>6</sub>	Units
A <sub>0</sub>	641.9	593.6	593.6	556.0	540.7	
A <sub>1</sub>	4094.1	4206.4	4206.4	4422.0	4514.1	kJ.mol <sup>-1</sup>
A <sub>2</sub>	19105.9	19170.7	18979.2	19703.8	19713.4	
U <sub>ST</sub> B <sub>1</sub>	-4404.9	-4441.3	-4441.3	-4549.1	-4548.5	kJ.mol <sup>-1</sup>
E <sub>2</sub>	-19098.6	-19254.2	-18880.9	-19712.3	-19718.2	
C <sub>0</sub>	641.9	593.6	593.6	556.0	540.7	
C <sub>1</sub>	-310.8	-234.9	-234.9	-127.1	-34.4	kJ.mol <sup>-1</sup>
C <sub>2</sub>	7.3	-83.5	98.3	-8.5	-4.8	
( $\frac{\partial U_{ELEC}}{\partial a}$ ) <sub>a=a<sub>0</sub></sub> C <sub>a0</sub>	-74.0	-72.6	-72.6	-74.9	-101.8	
C <sub>a1</sub>	203.5	146.1	146.1	80.2	38.5	kJ.mol <sup>-1</sup>
C <sub>a2</sub>	-8.1	91.6	-38.0	28.0	7.9	Å <sup>-1</sup>
( $\frac{\partial U_{ELEC}}{\partial c}$ ) <sub>c=c<sub>0</sub></sub> C <sub>c0</sub>	-18.7	-	-	-17.2	-	
C <sub>c1</sub>	36.3	-	-	23.8	-	kJ.mol <sup>-1</sup>
C <sub>c2</sub>	2.3	-	-	-11.3	-	Å <sup>-1</sup>
U <sub>ad</sub>	39.5	41.2	35.4	47.3	58.9	kJ.mol <sup>-1</sup>
U <sub>ad</sub> /a <sub>0</sub>	-44.0	-50.2	-39.6	-49.9	-85.7	kJ.mol <sup>-1</sup>
U <sub>ad</sub> /c <sub>0</sub>	-9.1	-	-	-13.4	-	Å <sup>-1</sup>

continued over

Results

Table 4.10(ii) continued

Term	LiWF <sub>6</sub>	NaWF <sub>6</sub> (A)	NaWF <sub>6</sub> (B)	KWF <sub>6</sub>	CsWF <sub>6</sub> Units
$U_{qd}$	2.1	2.9	2.4	3.5	5.8 kJ.mol <sup>-1</sup>
$\partial U_{qd}/\partial a$	-3.4	-5.1	-3.9	-5.6	-11.8 kJ.mol <sup>-1</sup>
$\partial U_{qd}/\partial c$	-0.7	-	-	-1.4	- Å <sup>-1</sup>
$\bar{r}_M$	0.424	0.875	0.875	1.191	1.465 Å
$1^{++}_R$	0.0	0.6	0.0	0.1	0.2 kJ.mol <sup>-1</sup>

Results

resulting from the derivative with respect to the  $a$  direction being below that for the  $c$  at the left-hand ordinate). The curves for the two possibilities for the sodium salt are given in Figure 4.10(ii), the  $A$  curve being below the  $B$  at the left. The curves for the potassium salt are plotted in Figure 4.10(iii) ( $c$  below  $a$  at left) and the curve for the cesium salt in Figure 4.10(iv).

The intersection point in Figure 4.10(i) at  $q_P = -0.290$  makes possible the assignment:

$$U_{\text{POT}}(\text{LiVF}_6) = 651 \text{ kJ.mol}^{-1} \quad 4.10(\text{ii})$$

that in Figure 4.10(iii), at  $q_P = -0.110$ :

$$U_{\text{POT}}(\text{KVF}_6) = 541 \text{ kJ.mol}^{-1} \quad 4.10(\text{iii})$$

These are the only two intersection points that can be used for assignment and so the value:

$$q_P = -0.20 \quad 4.10(\text{iv})$$

is adopted. This leads to:

$$U_{\text{POT}}(\text{CsVF}_6) = 528 \text{ kJ.mol}^{-1} \quad 4.10(\text{v})$$

## Results

Figure 4.10(ii) Lattice energy of sodium hexafluorotungstate.

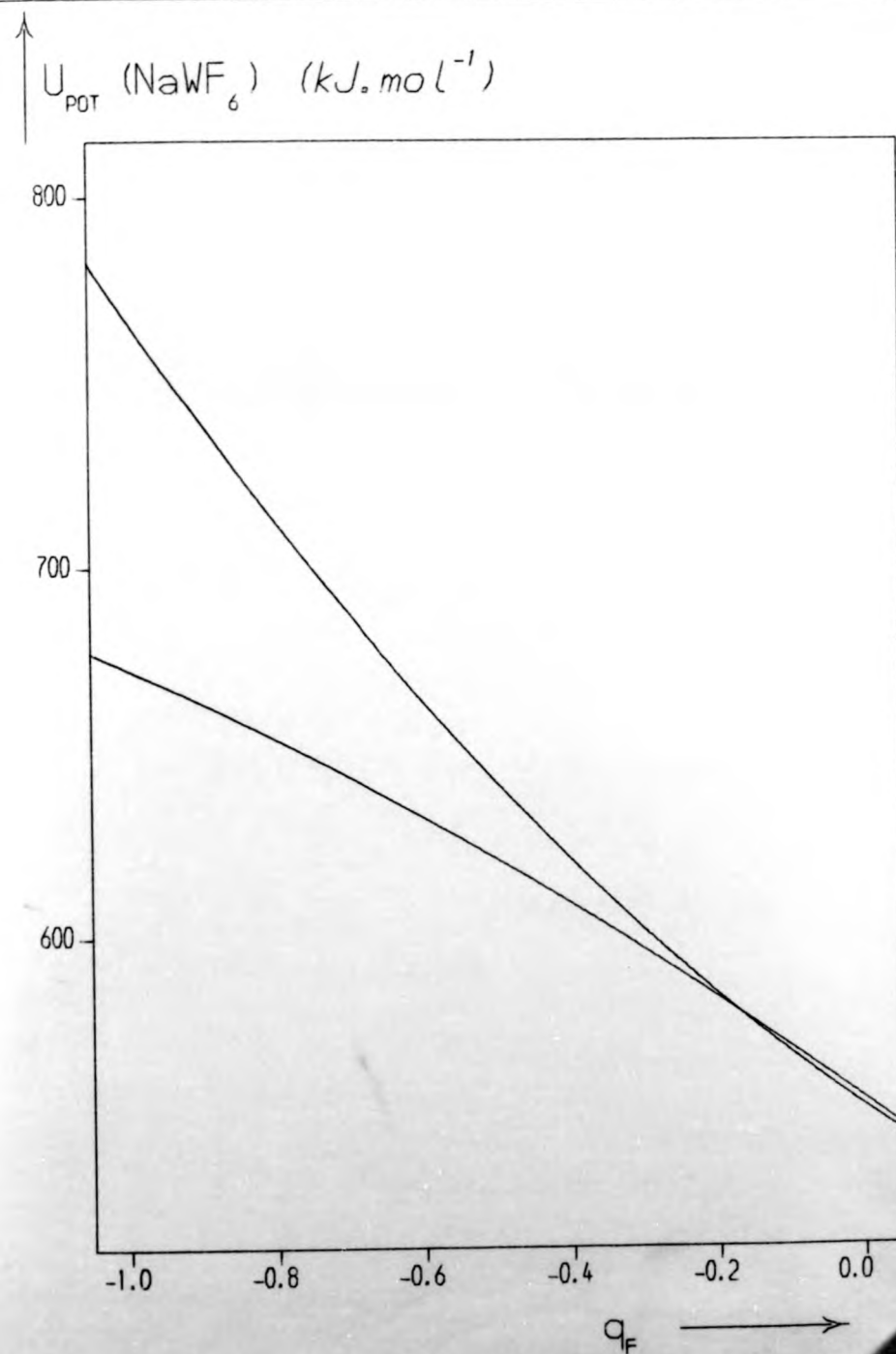
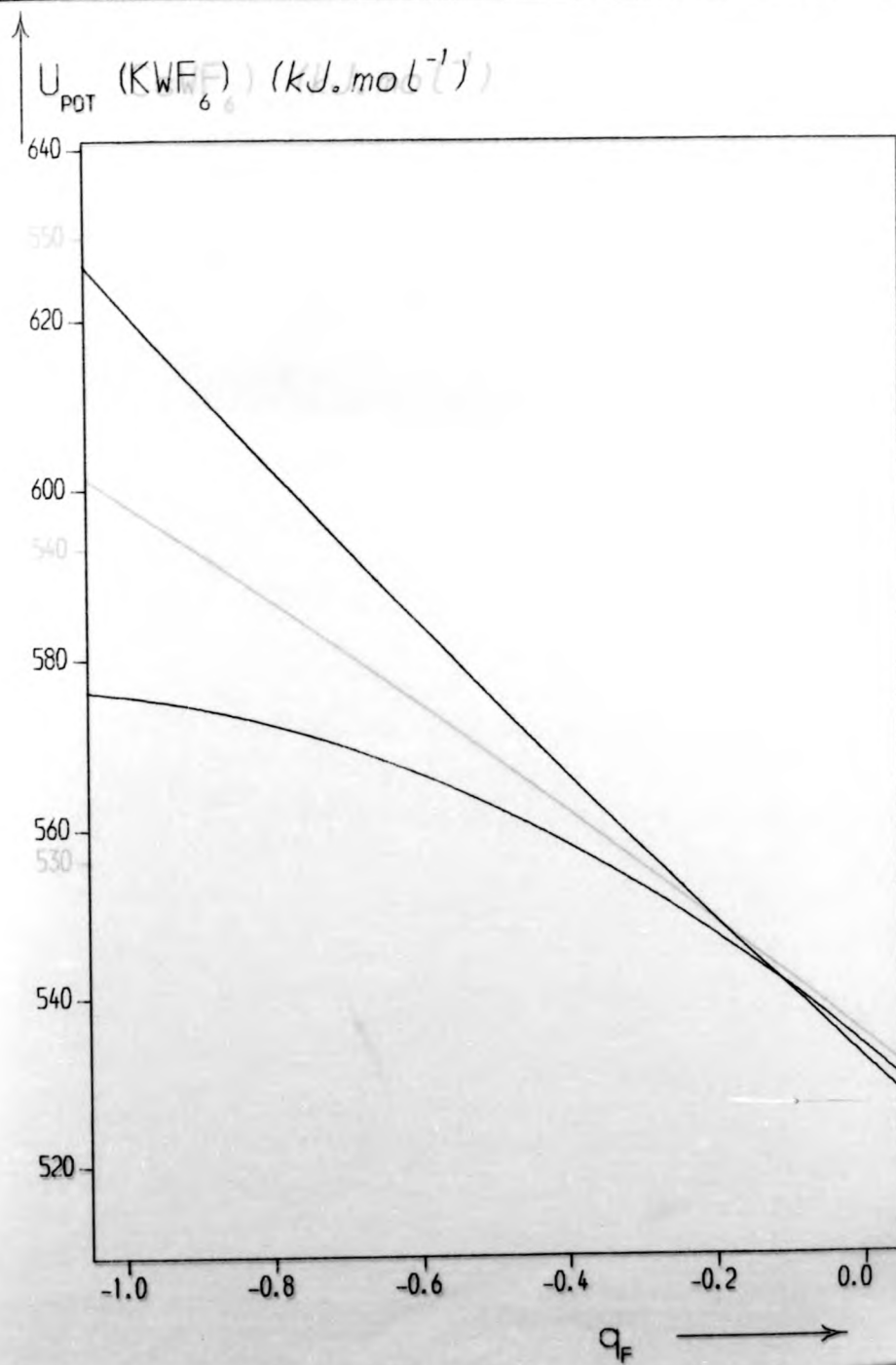


Figure 4.10(iii) Lattice energy of potassium hexafluorotungstate.



The two different structures of the sodium salt give virtually equivalent lattice energies at this charge distribution (the curves in Figure 4.10(ii) intersect at  $q_F = -0.176$ ). A third possibility suggested by Peacock (1978) is a disordered form, where the fluorine atoms are statistically distributed over a set of 96 positions. This is intermediate between the extremes for which calculations have been performed and so it seems reasonable to tentatively assign the lattice energy of this salt at the intersection of the curves, so:

$$U_{\text{POT}}(\text{NaWF}_6) = 579 \text{ kJ.mol}^{-1} \quad 4.10(\text{vi})$$

At greater charge distributions than the intersection the  $\beta$  form is more stable, at lower the  $\alpha$ . The disordered form is presumably intermediate of the two.

At the charge distribution of Equation 4.10(iv) the average value for the basic radius of the fluorine atoms (with standard deviation) is:

$$\bar{r}_F = 0.90 \pm 0.02 \text{ \AA} \quad 4.10(\text{vii})$$

The thermochemical cycle that relates the lattice

## Results

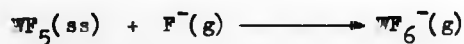
enthalpy to the enthalpy of formation of the gaseous anion implies, for monatomic W:

$$\Delta H_F^\circ(WF_6^-)(g) = U_{POT}(WF_6) + \Delta H_F^\circ(WF_6)(c) - \Delta H_F^\circ(W^+)(g) + \frac{1}{2}RT \quad 4.10(viii)$$

Using the thermochemical data in Table 4.10(iii) enables Figure 4.10(v) to be plotted, and from the figure this assignment (with standard deviation) can be made.

$$\Delta H_F^\circ(WF_6^-)(g) = -2218 \pm 35 \text{ kJ.mol}^{-1} \quad 4.10(ix)$$

The fluoride ion affinity of tungsten pentafluoride ( $\Delta H_F^\circ(ss)$ ) is the enthalpy change for the process:



Using the data  $\Delta H_F^\circ(F^-)(g) = -270.7$  (Cox et al (1972)),  $\Delta H_F^\circ(WF_5)(c) = -1584 \text{ kJ.mol}^{-1}$  (Barnes et al (1974)) and the sublimation enthalpy of  $WF_5$ , taken from Burgess, Haigh and Peacock (1971), allows the assignments:

$$\Delta H_F^\circ(g) = -461 \text{ kJ.mol}^{-1} \quad 4.10(x)$$

$$\Delta H_F^\circ(o) = -363 \text{ kJ.mol}^{-1} \quad 4.10(xi)$$

## Results



Figure 4.10(v) Enthalpy of formation of the gaseous hexafluorotungstate ion.

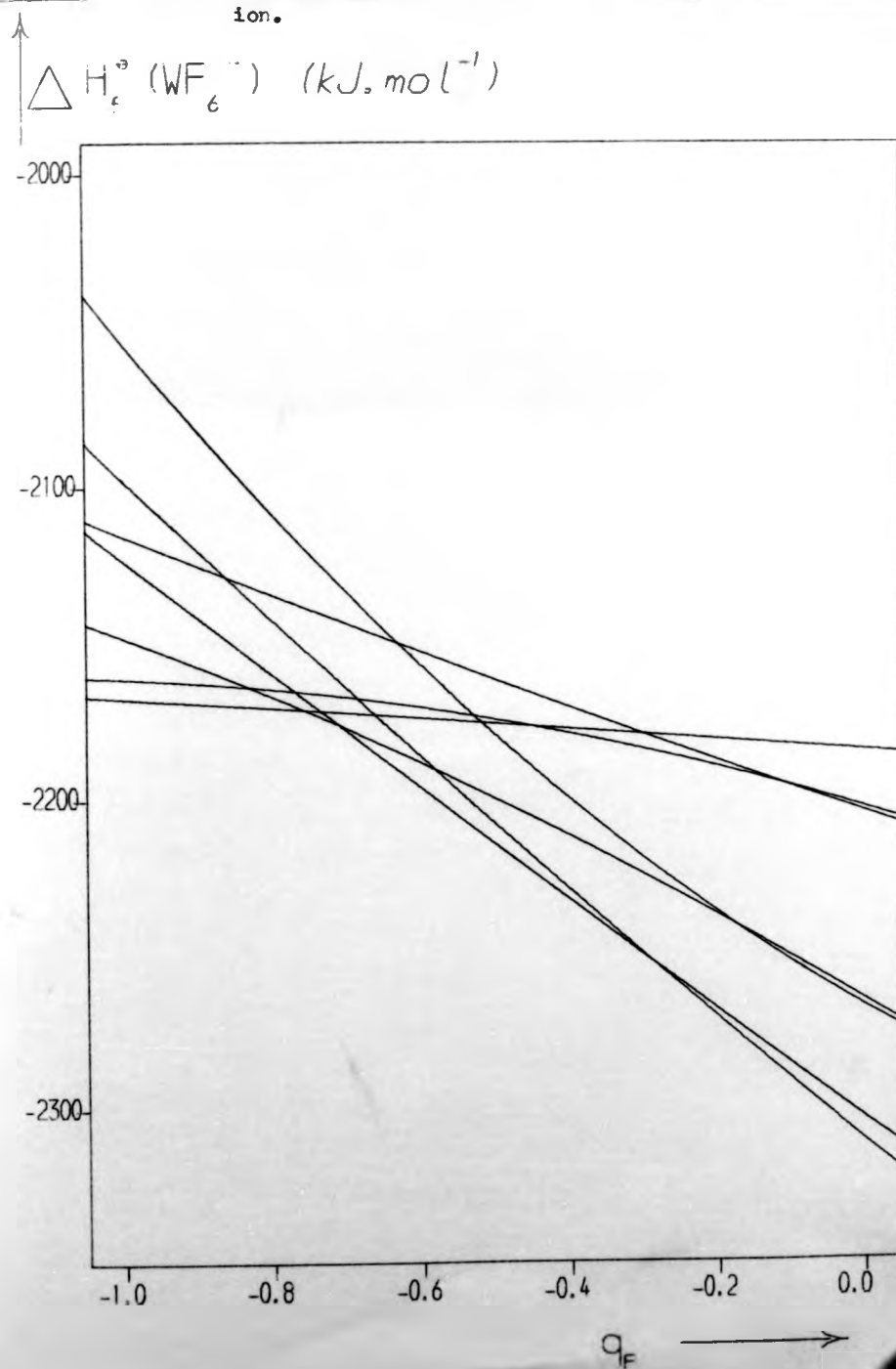


Table 4.10(iii) Thermochemical data for hexafluorotungstate(V) salts.

Salt	$\Delta H_f^\circ(\text{MWF}_6)(\text{c})$ a	$\Delta H_f^\circ(\text{M}^+)(\text{g})$ b
$\text{LiWF}_6$	-2219	687.1
$\text{NaWF}_6$	-2211	609.8
$\text{KWF}_6$	-2224	514.2
$\text{CsWF}_6$	-2253	452.3

a taken from Burgess and Peacock(1977)

b Stull and Prophet(1971)

#### Results

The electron affinity of gaseous tungsten hexafluoride ( $EA(WF_6)$ ) can be estimated, by employing the data  $\Delta H_f^\circ(WF_6)(g) = -1721.5 \text{ kJ.mol}^{-1}$  (Barnes et al (1974)), to be:

$$EA(WF_6) = -497 \text{ kJ.mol}^{-1} \quad 4.10(xii)$$

Burgess and Peacock (with their co-workers) (1971, 1974, 1977) use the Born-Mayer equation for the estimation of lattice energies which they found to be somewhat lower than those obtained here. The thermochemical parameters they quote are consequently fairly different to the above, illustrating the unreliability of the less rigorous methods of calculation (they used similar unit cell details for the salts to those used in this work). Burgess and Peacock (1977) have used a more complete approach to the calculation of lattice energies for the salts considered here. However this is without use of the energy minimisation condition. Unfortunately they do not quote results for the lattice energies obtained by these calculations but their thermochemical parameters indicate a still substantial disagreement with those reported here. The charge distribution they assign ( $q_F = -0.22$ ) does however agree well with the value found in this work.

## Results

Experimental determinations of the electron affinity of tungsten hexafluoride disagree not only within themselves but also with the value found above. Cooper and Compton (1974) report a value of  $-434 \text{ kJ.mol}^{-1}$  from crossed beam work, this agreeing much better with lattice energy studies than the figure of  $-356 \text{ kJ.mol}^{-1}$  obtained from collision ionisation by Disperf and Lacmann (1977).

The tentatively assigned crystal structures used appear to have not been found obviously at fault by this study. However the reasonably large range of results for thermochemical parameters produced could indicate a certain lack of accuracy either in the structures or thermochemical data. The disagreement found with the limited experimental values of the electron affinity of tungsten hexafluoride is thought not necessarily to reflect that a poor value has been assigned above.

It is hoped in the near future that accurate crystal structure data will be available for these salts so that assignments can be made with more confidence.

## Results

## 5. Conclusions

The major conclusion from Section 4 must be that the method for calculating the lattice energy of complex salts proposed in Section 2.7 appears to produce generally reliable and consistent results. This conclusion is drawn by considering the results obtained for both the lattice energies and the thermochemical parameters of the many compounds treated, involving a variety of complex ions.

Some other specific concluding remarks also seem necessary, concerning possible remaining sources for error in the calculations and points emerging from the results obtained.

The effect of the deviations of the calculated lattice energy from the 'true' value ( $\Delta_1$  and  $\Delta_2$ , introduced in Section 1.4) has been mostly minimised by suitable choice of salts. Generally only alkali metal and ammonium ion salts are considered where covalency and polarisation should be small, and these are the major contributors to any deviation. The second term is avoided by disregarding crystal structures that show greatly distorted ions. Alkaline earth and chalcogenide ion salts, for which

## Conclusions

covalency is possibly appreciable, are considered in only two studies. In the calculations concerning the peroxide ion no firm evidence for covalency is exhibited. However the deviations make the assignment of 'constant' basic radii, in Section 4.2, for these ions difficult. The general conclusion is that where possible multiply charged ions should be avoided, to reduce the effects of polarisation and possible covalency.

The results obtained by 'empirical' equations (Section 1.5) although generally approximately equal to those obtained from the 'non-empirical' approach given here do differ markedly in some cases, particularly for hexahalometallate(IV) and peroxide salts. There appears to emerge no general rule for predicting when empirical equations will produce reliable results, and when not. This conclusion implies that empirical equations should be used with some caution, and that they shouldn't be considered for use when sufficient data is available for the implementation of more rigorous approaches.

Section 2.4 states with clarity that methods of calculating dispersion energies are far from reliable. In Section 2.8 it is shown how possible errors in this term are reduced by the energy minimisation condition. However this

#### Conclusions

mechanism is **not** claimed to free the calculations of error resulting from this term. The work of Yuen et al (1977) has found disturbingly large dispersion coefficients for calcium carbonate by fitting a potential to the crystal structure data, using the energy minimisation condition. The large difference between the dispersion coefficients found in this study and those predicted by the theories of Section 2.4 is very unsatisfactory and it is hoped that it can be resolved soon. Insufficient calculations have yet been performed by Yuen et al's approach to say whether the difference found is universal or specific.

The major criticism which has been leveled against the potential chosen in Section 2 is the adoption of a constant value for the repulsion exponent. It has been shown (Section 2.3) that possible errors introduced by this assumption are somewhat reduced by the consideration of an energy minimum. The assumption is forced upon us by the lack of accurate, or usually any, compressibility data for complex salts. The value adopted has however been obtained from calculations on alkali halides, and so it can be expected to be approximately correct for systems where alkali metal to halogen contacts predominate, which is the case for a majority of the salts considered. Consequently the repulsion exponent should not be considered as a major possible source

#### Conclusions

of error in the majority of this work, and errors should still be only small (Section 2.8) for systems where a reasonable difference in value is possible (e.g. metal peroxides).

Sections 2.8 and 4.2 show well that the 'known' and 'unknown' basic radii have an exceptional tendency for balancing one another, which is a property of the type of equation in which they appear. Consequently the choice of radii used to calculate the 'unknown' seems to be not of great importance, as long as some sort of chemically reasonable value is used (i.e. solution of the equations is not precluded). However in order to treat basic radii for partial complex ions as approximately constant over a series of salts it is necessary to use a consistent set of counter ion radii. Approximate values for radii are assigned in Section 4.2, and if these are used in calculations the computed radius can be treated as in some ways an ion property, although great caution must still be exercised.

The cyanide ion calculations (Section 4.3) show how the method can be adapted, in special circumstances, to deal with ions which are not well approximated by a collection of spheres. The results obtained in this study show the adaption to be justified, but the loss of the large volume

#### Conclusions



of data as final results found for the straight application of the method makes the assignment of values difficult. The improvement of the crystal structure of lithium cyanide would lead to more confident assignments in Section 4.3 as the curve resulting should provide a discriminant.

The studies on hexahalometallate(IV) ions has been a major part of this research. Much valuable comparative data has been calculated for ions, many not previously considered by lattice energy studies. The seemingly steady flow of further experimental crystal structures and thermochemical data should be used in future calculations to extend the results, providing a frequent updating of this work.

Two points emerge from an overall view of the combination of the lattice energies into thermochemical cycles where they are related to the enthalpies of formation of the gaseous ions. The enthalpy of formation of the gaseous cesium ion taken from Stull and Prophet (1971) appears inconsistent with the other data over the majority of cesium salts considered. This study appears to predict a value about  $10 \text{ kJ.mol}^{-1}$  higher than that used, and as the value is still under review this correction seems likely to be reasonably valid. Secondly, studies on some ammonium salts seem to indicate a contribution to the lattice

#### Conclusions

enthalpy of some  $20-30 \text{ kJ.mol}^{-1}$  from some factor not taken into account by the potential used. In these salts (cyanide, azide, difluoride and fluoride) a strong possibility of hydrogen bonding between adjacent ions exists and this is suggested as the cause of the deviation.

The overall impression of this study is that the method evolved should be of general use to chemists in their studies on inorganic energetics, in that it provides a rationalization of lattice energy calculation for complex salts in the framework of a simple to use computer program.

#### Conclusions

## 6. References

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- Alcock N.W. and Jenkins H.D.B., *J.C.S. Dalton*, 1207 (1974)
- Archibald T.W. and Sabin J.F., *J. Chem. Phys.*, **55**, 1821 (1971)
- Baenziger N.C., *Acta Cryst.*, **4**, 216 (1951)
- Baburov V.G., *Trudy Inst. Khim. Uralskogo Feliata ANSSR*, No 7, 27 (1953)
- Barnes D.S., Pedley J.B., Kirk A., Winsor F. and Heath L.C., *CATCH Tables, (Cr. Mo and W Compounds)*, University of Sussex (1974)
- Basolo F. and Pearson R.G., "Mechanisms of Inorganic Reactions", Wiley, New York (1958)
- Baughan E.C., *Trans. Faraday Soc.*, **55**, 736 (1959)
- Bell J.D., Hall D. and Waters T.N., *Acta Cryst.*, **21**, 440 (1966)
- Berkowitz J., Chupka W.A. and Walter T.A., *J. Chem. Phys.*, **50**, 1497 (1959)
- Bertaut E.F., *J. Phys. Radium*, **13**, 497 (1952)
- Bertaut E.F., *J. Phys. Chem. Solids*, **39**, 97 (1978)
- Berthold H.J. and Jakobson G., *Angew. Chem.*, **76**, 497 (1964)
- Bijvoet J.M. and Lely J.A., *Rec. Trav. Chim.*, **59**, 908 (1940)
- Blake A.B., Quantum Chemistry Program Exchange, Prog. 222,

Indiana University (1973)

Blake A.B., **J.C.S. Dalton**, 1331 (1977)

Bode H. and Telfer G., **Z. Anorg. Allg. Chem.**, 283, 18  
(1956)

Born M. and Lande A., **Verhandl. dent. Physik Ges.**, 20,  
210 (1918)

Born M., "Problems of Atomic Dynamics", Lectures to M.I.T.  
(1926)

Born M. and Mayer J.E., **Z. Physik**, 75, 1 (1932)

Brill T.B., Gearhart R.C. and Welsh M.A., **J. Mag. Reson.**,  
13, 27 (1974)

Brown I.D., **Canad. J. Chem.**, 42, 2758 (1964)

Brown T.L., McDougle W.G. and Kent L.G., **J. Amer. Chem.  
Soc.**, 92, 3645 (1970)

Brunton G., **Mater. Res. Bull.**, 6, 555 (1971)

Brunton G., **Acta Cryst.**, B29, 2294 (1973)

Buchner E.H., **Kolloid Z.**, 75, 1 (1936)

Buchner E.H., **Rec. Trav. Chim.**, 69, 329 (1950)

Burgess J., Haigh I. and Peacock R.D., **Chem. Comm.**, 977  
(1971)

Burgess J., Haigh I., Peacock R.D. and Taylor P., **J.C.S.  
Dalton**, 1064 (1974)

Burgess J. and Peacock R.D., **J. Fluorine Chem.**, 10, 479  
(1977)

Busing W.R., **Trans. Amer. Cryst. Ass.**, 6, 57 (1970)

Busing W.R., **J. Chem. Phys.**, 57, 3008 (1972)

- Choi C.S. and Prince F., **J. Chem. Phys.**, **64**, 4510 (1976)
- Choi C.S., **Energetic Mat.**, **1**, 97 (1977)
- Cooper C.D. and Compton P.N., **Bull. Am. Phys. Soc.**, **19**,  
1106 (1974)
- Cotton F.A. and Johnson H.F.G., **Inorg. Chem.**, **3**, 781  
(1964)
- Coulter L.V., Fitzer K.S. and Latimer W.M., **J. Amer. Chem.  
Soc.**, **62**, 2845 (1940)
- Cox J.D., Padley J.B., Kirk A., Seilman S. and Heath L.G.,  
CATCH Tables, (Halogen compounds), University of  
Sussex (1972)
- Das A.K. and Brown R.D., **Canad. J. Chem.**, **44**, 939 (1966)
- Decker D.L., Beyerlein R.A., Fault G. and Worlton T.G.,  
**Phys. Rev.**, **B10**, 3564 (1974)
- De Jonge R.M., **J. Inorg. Nucl. Chem.**, **38**, 1821 (1976)
- Demrynck J., Veillard A. and Vinot G., **Chem. Phys. Lett.**,  
**10**, 522 (1971)
- Dispert H. and Lachmann K., **Chem. Phys. Lett.**, **45**, 311  
(1977)
- Dixon H.P., Jenkins H.D.B. and Waddington T.C., **Chem.  
Phys.**  
**Lett.**, **10**, 600 (1971)
- Dixon H.P., Jenkins H.D.B. and Waddington T.C., **J. Chem.  
Phys.**, **57**, 4388 (1972)
- Efimov A.I. and Beloruka L.P., **Russ. J. Inorg. Chem.**,  
**12**, 792 (1967)

- Eisenschitz F. and London F., *Z. Physik*, **60**, 491 (1930)
- Elder P., Ferguson J.F., Gainsford G.J., Hickford J.H. and Penfold B.R., *J. Chem. Soc. A*, 1423 (1967)
- Elliott N. and Hastings J., *Acta Cryst.*, **14**, 1018 (1961)
- Evjen F.M., *Phys. Rev.*, **39**, 675 (1932)
- Ewald P.P., *Ann. Physik*, **64**, 253 (1921)
- Ewald P.P., *Göttinger Nachr., Math.-Phys. Kl. II*, **3**, 55 (1937)
- Frank F.C., *Phil. Mag.*, **41**, 1287 (1951)
- Frech K. and Decius J.C., *J. Chem. Phys.*, **51**, 5315 (1969)
- Frevel L.K., *Z. Krist.*, **94**, 197 (1936)
- Fumi F.G. and Tosi M.P., *J. Phys. Chem. Solids*, **23**, 395 (1962)
- Fumi F.G. and Tosi M.P., *Lattice Dyn., Proc. Int. Conf., Copenhagen*, 281 (1963)
- Fumi F.G. and Tosi M.P., *J. Phys. Chem. Solids*, **25**, 31 (1964)
- Fumi F.G. and Tosi M.P., *J. Phys. Chem. Solids*, **25**, 45 (1964)
- Gearhart R.C., Ph.D. Thesis, University of Delaware (1972)
- Gearhart R.C., Beck J.D. and Wood R.H., *Inorg. Chem.*, **14**, 2413 (1975)
- Gelbman P. and Westland A.D., *J.C.S. Dalton*, 1599 (1974)
- Gilbert I.L., *J. Chem. Phys.*, **49**, 2640 (1968)
- Glyshko V.P., "Thermochemical Constants of Compounds", **7**,

- Akad. Nauk., USSR, Moscow (1974)
- Goltschmidt V.M., *Skrifter Norske Videnskaps-Akad. Oslo*,  
*Math.-Nat. Kl. No. 2* (1926)
- Golutvin Y.I., Maslennikova E.G., Li A.W., Safonov V.V. and  
Korshunov B.G., *Russ. J. Phys. Chem.*, **48**, 1604  
(1974)
- Goodcliffe A.L., Jenkins H.D.B., Martin S.V. and Waddington  
I.C., *Mol. Phys.*, **21**, 76 (1971)
- Gora I., Downs D.S., Keemey P.J. and Sharma J., *Energetic  
Mat.*, **1**, 193 (1977)
- Gray P. and Waddington I.C., *Proc. Roy. Soc.*, **A235**,  
481 (1956)
- Gross F., Haymann C. and Bingham J.J., *Trans Faraday Soc.*,  
**62**, 2386 (1956)
- Grundy H.D. and Brown R.D., *Canad. J. Chem.*, **48**, 1151  
(1970)
- Halliwel H.f. and Nyburg S.C., *Trans Faraday Soc.*, **59**,  
1126 (1963)
- Hanic F., *Chem. Zvesti*, **20**, 738 (1966)
- Harris F.E. and Monkhorst H., *Chem. Phys. Lett.*, **4**,  
181 (1969)
- Hartley F.R., *Nature Phys. Sci.*, **239**, 75 (1972)
- Hazell A.C., *Acta Chem. Scand.*, **20**, 168 (1966)
- Herron J.T. and Dibler V.H., *J. Amer. Chem. Soc.*, **82**,  
1555 (1960)
- Herzig P., Kuzmany P. and Neckel A., Unpublished work (1970)

Hillier I.H. and Saunders V.R., **Mol. Phys.**, **23**, 449  
(1972)

Hopkins K.G.G., Ph.D. Thesis, University of Hull (1970)

Huggins M.L. and Mayer J.E., **J. Chem. Phys.**, **1**, 643  
(1933)

Huggins M.L., **J. Chem. Phys.**, **5**, 143 (1937)

Huggins M.L. and Sakamoto Y., **J. Phys. Soc. Japan**, **12**,  
241 (1957)

Jansen L. and McGinnies R.T., **Phys. Rev.**, **101**, 1321  
(1956a)

Jansen L. and McGinnies R.T., **Phys. Rev.**, **104**, 961  
(1956b)

Jansen L., **Physica**, **23**, 599 (1957)

Jansen L. and Lombardi E., **Phys. Rev. Lett.**, **12**, 11  
(1964)

Jansen L. and Lombardi E., **Phys. Rev.**, **151**, 694 (1966)

Jaswal S.S. and Sharma I.P., **J. Phys. Chem. Solids**, **34**,  
509 (1973)

Jenkins H.D.B., **Chem. Phys. Lett.**, **9**, 473 (1971)

Jenkins H.D.B., **Chem. Phys. Lett.**, **20**, 155 (1973)

Jenkins H.D.B. and Waddington I.C., **Chem. Phys. Lett.**,  
**31**, 369 (1975a)

Jenkins H.D.B. and Waddington I.C., **J. Chem. Phys.**, **62**,  
4586 (1975b)

Jenkins H.D.B., **J.C.S. Faraday II**, **72**, 1569 (1976a)

Jenkins H.D.B., **Inorg. Chem.**, **15**, 241 (1976b)



Jenkins H.D.B., Herzig P. and Neckel A., **J. Phys. Chem.**,

**80**, 1608 (1976)

Jenkins H.D.B. and Morris D.F.C., **Mol. Phys.**, **32**, 231

(1976)

Jenkins H.D.B. and Pratt K.F., **J. Inorg. Nucl. Chem.**,

**38**, 1775 (1976a)

Jenkins H.D.B. and Pratt K.F., "Repulsion energy and 'basic'

radii for ions...". Res. report suppl. No.1 (1976b)

Jenkins H.D.B. and Smith B.T., **J.C.S. Faraday I**, **72**,

353 (1976)

Jenkins H.D.B., **J. Phys. Chem.**, **81**, 850 (1977)

Jenkins H.D.B. and Morris D.F.C., **Mol. Phys.**, **33**, 663

(1977a)

Jenkins H.D.B. and Morris D.F.C., **Phil. Mag.**, **35**,

1091 (1977b)

Jenkins H.D.B. and Pratt K.F., **Proc. Roy. Soc.**, **A356**,

115 (1977a)

Jenkins H.D.B. and Pratt K.F., **J. Chem. Res.**, 64 (1977b)

Jenkins H.D.B. and Pratt K.F., **J. Phys. Chem. Solids**,

**38**, 573 (1977c)

Jenkins H.D.B. and Pratt K.F., **J.C.S. Faraday II**, 812

(1977d)

Jenkins H.D.B., Pratt K.F. and Waddington T.C., **J. Inorg.**

**Nucl. Chem.**, **39**, 213 (1977)

Jenkins H.D.B. and Pratt K.F., **Comp. Phys. Comm.**, **13**,

341 (1978a)

- Jenkins H.D.B. and Pratt K.F., **J.C.S. Faraday II**, **74**,  
968 (1978b)
- Jenkins H.D.B. and Pratt K.F., **Adv. Inorg. Chem.**  
**Radiochem.**, **22**, at the printers (1978c)
- Jenkins H.D.B. and Pratt K.F., **Prog. Solid State Chem.**,  
accepted for publication (1978d)
- Jensen A.T. and Rasmussen S.E., **Acta Chem. Scand.**, **9**,  
708 (1955)
- Jorgensen Chr. K., Horner S.M., Hatfield W.E. and Tyree Jrr.  
F.Y., **Int. J. Quant. Chem.**, **1**, 191 (1957)
- Jorgensen Chr. K., **Prog. Inorg. Chem.**, **4**, 73 (1962)
- Jorgensen Chr. K., **Adv. Chem. Phys.**, **5**, 33 (1963)
- Jorgensen Chr. K., "Oxidation Numbers and Oxidation States",  
Springer-Verlag, Berlin (1969)
- Kaatz T. and Marcovich M., **Acta Cryst.**, **21**, 1011 (1966)
- Kapustinskii A.F., **Z. Physik Chem. (Leipzig)**, **B22**,  
257 (1933)
- Kapustinskii A.F., **J. Phys. Chem. (USSR)**, **5**, 59 (1943)
- Kapustinskii A.F., **Acta Physicochim. (USSR)**, **18**, 370  
(1943)
- Kapustinskii A.F. and Yatsimirskii K.B., **Zh. Obshch.**  
**Khim.**, **19**, 2191 (1949)
- Kapustinskii A.F., **Quart. Rev.**, **10**, 283 (1956)
- Kazarnovskii I.A. and Raikhshein S.I., **Russ. J. Phys.**  
**Chem.**, **21**, 245 (1947)
- Kennedy C.D. and Peacock R.D., **J. Chem. Soc.**, 3392 (1963)

- Kurcil'kov D.V. and Efimov A.I., *Probl. Sovrem. Khim. Khorg. Soedin.*, Leningrad Gos. Univer. No.1, 215 (1966)
- Kubo M. and Nakamura T., *Adv. Inorg. Chem. Radiochem.*, **8**, 250 (1966)
- Ladd M.F.C. and Lee W.H., *Trans. Faraday Soc.*, **54**, 34 (1958)
- Ladd M.F.C., *Trans. Faraday Soc.*, **65**, 2712 (1969)
- Lal D. and Westland A.D., *J.C.S. Dalton*, 2505 (1974)
- Lalanchette R.A., Elliott N. and Bernal I., *J. Cryst. Mol. Struct.*, **2**, 143 (1972)
- Lely J.A. and Bijvoet J.M., *Rec. Trav. Chim.*, **61**, 244 (1942)
- Lely J.A. and Bijvoet J.M., *Rec. Trav. Chim.*, **63**, 39 (1944)
- Lister R.L. and Flengas S.N., *Canad. J. Chem.*, **42**, 1102 (1964)
- London F., *Z. Physik*, **63**, 245 (1930)
- London F., *Z. Physik Chem. (Leipzig)*, **B11**, 222 (1930)
- Madelung E., *Physik Z.*, **19**, 524 (1918)
- Mairesse G., Barbier P., Wignacourt J.P. and Baert F., *Cryst. Struct. Comm.*, **6**, 15 (1977)
- Mairesse G., Barbier P. and Wignacourt J.P., to be published (1978a)
- Mairesse G., Barbier P. and Wignacourt J.P., *Acta Cryst.*, in the press (1978b)
- Mairesse G., Barbier P., Wignacourt J.P., Rutbens A. and

- Wallart F., **Canad. J. Chem.**, in the press (1978)
- Margenau H., **Phys. Rev.**, **38**, 747 (1931)
- Margenau H., **Rev. Mod. Phys.**, **11**, 1 (1939)
- Margenau H. and Kestner N.R., "Theory of Intermolecular Forces", Pergamon (1971)
- Marr H.E. and Stanford Jnr. R.H., **Acta Cryst.**, **15**, 1313 (1962)
- Mayer J.E., **J. Chem. Phys.**, **1**, 270 (1933)
- Michael A.J., **J. Chem. Phys.**, **51**, 5737 (1969)
- Moews P.C., **Inorg. Chem.**, **5**, 5 (1966)
- Morris D.F.C., **Struct. & Bonding**, **4**, 63 (1968)
- Morss L.R. and Fuger J., **Inorg. Chem.**, **8**, 1433 (1965)
- Mueller A., **Proc. Roy. Soc.**, **A154**, 624 (1936)
- Muller U., **Z. Anorg. Allg. Chem.**, **392**, 159 (1972)
- Murfitt R.R., Ph.D. Thesis, University of Rochester (1971)
- Narayan R., **J. Phys. Chem. Solids**, **38**, 1097 (1977)
- Neckel A. and Vinek G., **Z. Phys. Chem. (Frankfurt)**, **42**, 129 (1964)
- Neckel A. and Vinek G., **Z. Phys. Chem. (Frankfurt)**, **48**, 61 (1966)
- Neckel A., Vinek G. and Nowotny H., **Acta Chim. Acad. Sci. Hung.**, **51**, 193 (1967)
- Neckel A., Kuzmany P. and Vinek G., **Z. Naturforsch.**, **A26**, 561 (1971a)
- Neckel A., Kuzmany P. and Vinek G., **Z. Naturforsch.**, **A26**, 569 (1971b)

- Neckel A., Herzig P. and Jenkins H.D.B., *J. Phys. Chem.*,  
80, 1608 (1976)
- Neckel A. and Herzig P., *Acta Cryst.*, A33, 819 (1977)
- Noyes R.M., *J. Amer. Chem. Soc.*, 84, 513 (1962)
- Pauling L., *Proc. Roy. Soc.*, A114, 191 (1927)
- Pauling L., *Z. Krist.*, 67, 377 (1928)
- Pauling L., "The Nature of the Chemical Bond", 3rd. Edn.,  
Oxford (1960)
- Pavlyuchenko M.M. and Popova T.I., *Akad. Nauk Belo-Russ.*  
*SSR Dokl.*, 7, 174 (1963a)
- Pavlyuchenko M.M. and Popova T.I., *Akad. Nauk Belo-Russ.*  
*SSR Dokl.*, 7, 456 (1963b)
- Peacock R.D., Private communication to H.D.B. Jenkins  
(1977-8)
- Pfaiffer H.G., Ph.D. Thesis, California Inst. of Tech.  
(1948)
- Phillips C.S.G. and Williams R.J.P., "Inorganic Chemistry",  
Vol. 1, Ch. 5 (1965)
- Pirenne J. and Kartheuser E., *Physica*, 30, 2005 (1964)
- Pitzer K.S., *adv. Chem. Phys.*, 2, 59 (1959)
- Pringle G.E. and Hoakes D.E., *Acta Cryst.*, B24,  
262 (1968)
- Pritchard H.O., *Chem. Rev.*, 52, 529 (1953)
- Quail J.W. and Rivett G.A., *Canad. J. Chem.*, 50,  
2447 (1972)
- Redlack A. and Grindlay J., *J. Phys. Chem. Solids*, 36,

73 (1975)

Refaeey K.M.A., *Int. J. Mass. Spect. Ion Phys.*, 21,  
21 (1976)

Refaeey K.M.A. and Franklin J.L., *J. Chem. Phys.*, 64,  
4810 (1976)

Rossini F.D., Wagman D.D., Evans W.H., Levine S. and Jaffe  
I., 'Selected Values of Chemical Thermodynamic  
Properties', Circulars 500, National Bureau of  
Standards, Washington (1952)

Sanderson R.T., "Chemical Bonds and Bond Energy", 2nd Ed.,  
Academic (1976)

Scheinert W. and Weiss A., *Z. Naturforsch.*, A31,  
1354 (1976)

Schlesinger E.C. and Hamilton W.C., *J. Chem. Phys.*, 44,  
2499 (1966)

Schwochan K., *Z. Naturforsch.*, 19, 1237 (1964)

Shiclovskii A.A. and Valkina K.V., *Russ. J. Phys. Chem.*,  
35, 142 (1961)

Siegel S., *Acta Cryst.*, 5, 683 (1952)

Slater J.C., *Phys. Rev.*, 32, 349 (1928)

Sommer H. and Hoppe R., *Z. Anorg. Allg. Chem.*, 429,  
118 (1977)

Stepin B.D., Plushchev V.E., Selivanova M.N. and  
Serebrennikova M.N., *Russ. J. Phys. Chem.*,  
42, 1255 (1968)

Stull D.R. and Prophet H., *JANAF Thermochemical Tables*, 2nd

- [d., National Bureau of Standards, Washington (1971)
- Swanson H.E., Fuyat R.K. and Ugrinic G.M., National Bureau  
of Standards, Monc., **25**, 1, 6 (1962)
- Swanson H.E., Fuyat R.K. and Ugrinic G.M., National Bureau  
of Standards, Monc., **25**, 2, 11 (1963)
- Templeton D.H., **J. Chem. Phys.**, **23**, 1629 (1955)
- Templeton D.H. and Jones R.C., **J. Chem. Phys.**, **25**,  
1062 (1956)
- Tessman J.H., Kahn A.H. and Shockley W., **Phys. Rev.**,  
**92**, 890 (1953)
- Thakur K.P., **Aust. J. Phys.**, **29**, 39 (1976)
- Tosi M.P., **Solid State Phys.**, **16**, 1 (1964)
- Tsintsius V.M. and Smirnova V.M., **Russ. J. Inorg. Chem.**,  
**14**, 1729 (1959)
- Vannerteng M.G., **Arkiv. For Kemi.**, **14**, 299 (1959)
- Vodovtso V.M., Suglobova I.G. and Chirkst D.F., **Sov.**  
**Radiochem.**, **16**, 205 (1974)
- Vodovtso V.M., Volkov V.A. and Suglobova I.G., **Sov.**  
**Radiochem.**, **16**, 364 (1974)
- Verweel H.J. and Bijvoet J.M., **Z. Krist.**, **100A**,  
201 (1938)
- Waddington T.C., Ph.D. Thesis, University of Cambridge  
(1955)
- Waddington T.C., **Trans. Faraday Soc.**, **54**, 25 (1958)
- Waddington T.C., **Adv. Inorg. Chem. Radiochem.**, **1**,  
159 (1959)

- Wajman D.D., Evans W.H., Halow I., Parker V.B., Bailey S.M.  
and Schumm P.H., NBS Technical Note 270-1, National  
Bureau of Standards, Washington (1965)
- Wajman D.D., Evans W.H., Parker V.B., Halow I., Bailey S.M.  
and Schumm P.H., NBS Technical Note 270-3, National  
Bureau of Standards, Washington (1968)
- Wajman D.D., Evans W.H., Parker V.B., Halow I., Bailey S.M.  
and Schumm P.H., NBS Technical Note 270-4, National  
Bureau of Standards, Washington (1969)
- Wajman D.D., Parker V.B. and Evans W.H., NBS Technical Note  
270-6, National Bureau of Standards, Washington (1971)
- Wajman D.D., Evans W.H., Parker V.B. and Schumm P.H.,  
Chemical Thermodynamic Properties of Compounds  
of Sodium, Potassium and Rubidium: An Interim  
Tabulation of Selected Values, National Bureau  
of Standards, Washington (1976)
- Webster M. and Collins P.H., **J.C.S. Dalton**, 588 (1963)
- Weerk J.W. and Harwig H.A., **J. Phys. Chem. Solids**, 36,  
763 (1975)
- Weerk J.W. and Harwig H.A., **J. Phys. Chem. Solids**, 38,  
1047 (1977a)
- Weerk J.W. and Harwig H.A., **J. Phys. Chem. Solids**, 38,  
1055 (1977b)
- Weise E. and Klemm W., **Z. Anorg. Allg. Chem.**, 272,  
211 (1953)
- Welsh W.A., Brill T.B., Thompson P.T. and Wood R.H.,



**Inorg. Chem., 13, 1797 (1974)**

- Williams D.E., **J. Chem. Phys.**, **43**, 4474 (1965a)  
Williams D.E., **Science**, **147**, 605 (1965b)  
Williams D.E., **J. Chem. Phys.**, **45**, 3770 (1966a)  
Williams D.E., **Acta Cryst.**, **21**, 340 (1966b)  
Williams D.E., **J. Chem. Phys.**, **47**, 4680 (1967)  
Williams D.E., **Acta Cryst.**, **A25**, 464 (1969)  
Williams D.E., **Trans. Amer. Cryst. Assoc.**, **6**, 21 (1970)  
Williams D.E., **Acta Cryst.**, **A27**, 452 (1971)  
Williams D.E., **Acta Cryst.**, **A28**, 84 (1972a)  
Williams D.E., **Acta Cryst.**, **A28**, 629 (1972b)  
Williams D.E., **Acta Cryst.**, **A30**, 71 (1974)  
Williams D.E. and Starr T.L., **Comput. Chem.**, **1**, 173  
(1977)  
Wilsdorf V.E., **Acta Cryst.**, **1**, 115 (1948)  
Winslow G.H., **J. Chem. Phys.**, **62**, 413F (1975)  
Wood R.H. and D'Orazio L.A., **J. Phys. Chem.**, **69**,  
2558 (1965)  
Wyckoff R.W.G., "Crystal Structures", 2nd Ed., Interscience,  
New York (1955)  
Yatsimirskii K.B., **Izvest. Akad. Nauk SSSR, Otdel Khim.**  
**Nauk**, 453 (1947)  
Yatsimirskii K.B., **Izvest. Akad. Nauk SSSR, Otdel Khim.**  
**Nauk**, 398 (1948)  
Yuen P.S., Murfitt R.R. and Collin R.L., **J. Chem. Phys.**,  
**61**, 2383 (1974)

Yuen P.S., Lister M.W. and Nyburg S.C., **J. Chem. Phys.**,

**68**, 1936 (1977)

Zalkin A., Forrester J.D. and Templeton D.H., **Acta Cryst.**,

**17**, 1408 (1964)

I N D E X

Absolute hydration enthalpy	22, 152, 166
Absorption spectrum	52
Acceleration of convergence	60
Acoustic energy	5
Alkali halides	22, 26, 28, 46, 87, 130
Alkali metal azides	155
Alkali metal difluorides	167
Alkali metal cyanides	26, 138
Alkali metal hexafluorotungstates	205
Alkali metal ions	50, 130
Alkali metal perchlorates	193
Alkali metal peroxides	201
Alkali metal tetrachloroaluminates	194
Alkaline earth metal halides	64
Alkaline earth metal ions	50, 132
Alkaline earth metal peroxides	201
Ammonium difluoride	167
Ammonium cyanide	138
Ammonium fluoride	174
Ammonium ion	136
Ammonium perchlorate	193
Ammonium salts	216
Ammonium tetrachloroaluminate	194
Anion-cation distance	65
Anisotropic ions	143
Anisotropy	161
Azide ion	49, 125, 154, 167
Basic radius	47, 50, 86, 94, 96, 106, 128, 129, 183, 196, 197, 215
Basic radius of the cyanide ion	139
Bertaut method	34, 43, 78, 111, 124, 179
Difluoride ion	49, 125, 144, 167
Bond angle	123
Bond energy	198
Bond length	123
Bonds	9
Born-Fajans-Haber cycle	6
Born-Haber lattice enthalpy	8
Born-Landé equation	67, 192
Born-Mayer equation	68, 210

Cesium chloride structure 28, 36  
 Chalcogenide ions 50, 132  
 Characteristic energy 54, 59, 93, 201  
 Charge density function 34, 76, 79, 107, 112  
 Charge distribution 10, 20, 40, 83, 87, 91, 97, 109,  
 127, 140, 149, 156, 161, 171, 177, 183, 195,  
 200, 210  
 Collision ionisation 211  
 Complex ion geometry 10  
 Complex ions 10, 17, 37, 40, 41, 62, 65, 69, 75,  
 83  
 Compressibility 71  
 Computer programs 75, 100  
 Computers 43  
 Constant rho 46  
 Constant-energy radius 47  
 Conventional hydration enthalpy 22, 152, 166  
 Convergence 32, 42, 110  
 Coordinate bond energy 189  
 Coordination number 110  
 Correlation forces 51  
 Covalency 10, 12, 204, 212  
 Crossed beam studies 211  
 Crystal radius 23  
 Crystal structure 12, 14, 49, 62, 64, 82, 127, 133,  
 194, 205  
 Cyanide ion 20, 137, 215  
 Differential ionisation energy 134  
 Dipole moment 39  
 Dipole-dipole dispersion energy 53, 92  
 Dipole-quadrupole dispersion energy 54, 92  
 Direct summation 60  
 Dispersion energy 18, 28, 36, 51, 66, 74, 81, 82, 87,  
 92, 94, 109, 139, 165, 170, 217  
 Dispersion forces 51  
 Dispersion model 96, 127, 181, 195, 206  
 d-orbital 38  
 Effective electron number 54, 59  
 Electron affinity 20, 210  
 Electron affinity of cyanide radical 153  
 Electron affinity of halogens 20  
 Electron cloud 9  
 Electron number 94  
 Electronegativity 150, 184  
 Electrostatic energy 18, 28, 29, 42, 66, 77, 81, 82, 87,  
 103, 111  
 Ellipsoidal repulsion model 154

Empirical equations	192
Energy minimisation	61, 126, 168
Enthalpy of formation, of aqueous ion	21
Enthalpy of formation, of gaseous ion	19
Enthalpy of hydration, of gaseous ion	19, 21
Enthalpy of sublimation	20, 188
Equation of state	61, 71
Equilibrium	44
Ewald method	34, 35, 37, 124
Exclusion principle	44
Exponential repulsion	45, 66
Field gradient	36, 40
Field strength	40
Finite crystal	39
Fluoride ion affinity	209
Fourier transformation	33, 34, 36, 39, 78, 112
Fractional coordinates	75
Gaussian charge density function	34, 35, 80
Goldschmidt ionic radius	17
Graph plotting	121
Halide ions	50, 130
Halogen dissociation energy	188
Heterolytic bond energy	188
Hexafluorogermanate ion	85
Hexafluorotungstate(V) ion	245
Hexagonal axes	85
Hexahalometallate(IV) ions	176, 216
Hexahalometallate(IV) salts	26, 38, 86
Homolytic bond energy	188
Huggins and Mayer repulsion energy	68, 154, 158, 170, 182, 196
Hydration enthalpy	152, 166, 187
Hydrocarbons	64
Hydrogen bond strength	174
Hydrogen bonding	156, 165, 173, 175, 217
Hydrogen positions	124
Infinite series	32
Input data	116
Interatomic distance	60
Internal energy	4
Intersection point	85, 90, 99, 110, 183, 197, 207
Inverse power repulsion	45, 67
Ionic charge	30, 47
Ionic polarisability	51
Ionic radius	23
Ionicity	127

- Ionisation potential 20, 59
- Isotropic assumption 128
- Jenkins and Waddington equation 73, 126, 154, 167, 176, 177, 199
- Jones-Dole equation 23
- Kapustinskii equation 69, 192, 200
- Kinetic energy 5
- LATEX 101, 126
- Ladd and Lee equation 69, 73, 201
- Lattice energy calculation, empirical 14
- Lattice energy calculation, non-empirical 14
- Lattice energy maximum 62, 74
- Lattice energy, definition 3
- Lattice energy, true and calculated 9, 212
- Lattice enthalpy 4, 19
- Lattice enthalpy, Born-Haber 8, 12
- Lattice parameter 114
- Lattice symmetry 43
- Least squares method 134
- Lithium tetrafluoroborate 64
- London forces 51
- MADDELLING DERIVATIVES 108, 127, 181, 195
- Madelung constant 31, 60, 78, 124, 133, 177
- Madelung energy 42, 77
- Many body forces 27
- Multipole moment expansion 11, 37, 124, 177
- Multipole moments 37, 106
- Nitrate ion 20
- Nitrite ion 20
- Non-spherical electron density 10
- Nuclear quadrupole resonance 194
- Overlap energy 107
- Overlap of Gaussians 35
- Pairwise interaction 27
- Perchlorate ion 193
- Periodicity 32, 34
- Peroxide ion 200
- Perturbation theory 44, 53
- Pleomorphic structures 138
- Polar crystals 40
- Polarisability 51, 54, 58, 93, 131, 139, 191, 201
- Polarising power of ions 161
- Potassium hexachloroplatinate 177

Potassium hexafluorogermanate	85
Proctor affinity of the cyanide ion	152
p-orbital	38
Quadrupole moment	39
Quadrupole-quadrupole dispersion energy	54
Quantum mechanical calculations	11, 19, 20, 45, 52, 149, 168, 176
Reciprocal lattice	34
Reciprocal lattice vector	78, 79, 110, 111
Refractive index	58
Repulsion energy	18, 28, 44, 67, 81, 32, 97, 94, 96
Repulsion envelope	49, 96, 128, 152
Repulsion exponent	72, 86, 87, 95, 131, 214
Repulsion model	96, 105, 120, 128, 142, 158, 170, 182, 202, 206
Repulsion summations	109
Repulsive potential	17
Rotation of cyanide ion	140
Self energy	42, 77
Self interaction energy	35
SOLV	110
Sodium chloride structure	17, 19, 28, 31, 36
Space group	62
Specific heat	5
Spherical charge distribution	86
Structure factor	78, 80
SUMS	62
Term-by-term calculation	18, 27
Tetrachloroaluminate ion	193
Thallium ion	136
Thallium salts	165
Thermochemical cycle	4, 128, 172, 186, 197, 202, 208
Thermochemical data	6
Thermochemical radii	16
Three body forces	27
Transition metal ions	10
Two body forces	27, 53
UELEC	81, 138
Unit cell lengths	62, 75
Unit cell volume	61, 78
Units	102
Valence electron number	47
Van der Waals forces	51

viscosity coefficient 23  
Zero point energy 5



**Appendix A**

Reprints of the available papers published in the  
scientific literature as part of this research.

# POLYMORPHIC TRANSITIONS IN CYANIDE CRYSTALS AND THE CALCULATION OF THE LATTICE ENERGIES OF CYANIDE SALTS. THERMODYNAMIC PARAMETERS FOR THE GASEOUS CYANIDE ION

H. D. B. JENKINS\* and K. F. PRATT

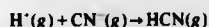
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(Received 8 November 1975)

**Abstract**—The lattice energies of the cubic and orthorhombic forms of NaCN and KCN are calculated. Using experimental data on the enthalpy of transition between the polymorphic forms we estimate:  $U_{\text{pot}}(\text{NaCN})_{\text{ortho}} = 732 \text{ kJ mol}^{-1}$ ,  $U_{\text{pot}}(\text{NaCN})_{\text{cubic}} = 729 \text{ kJ mol}^{-1}$ ,  $U_{\text{pot}}(\text{KCN})_{\text{ortho}} = 665 \text{ kJ mol}^{-1}$  and  $U_{\text{pot}}(\text{KCN})_{\text{cubic}} = 664 \text{ kJ mol}^{-1}$ . Using these results we estimate  $\Delta H_f^\circ(\text{CN}^-(g)) = 33 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{ion}}^\circ(\text{CN}^-(g)) = -326 \text{ kJ mol}^{-1}$ , the proton affinity of the gaseous  $\text{CN}^-$  ion to be  $-1434 \text{ kJ mol}^{-1}$  and the electron affinity of the cyanide radical to be  $402 \text{ kJ mol}^{-1}$ . The charge distribution we assign compares extremely well with quantum mechanical calculations.

## INTRODUCTION

THE ALKALI metal cyanides are cubic at room temperature (with the exception of LiCN, which is orthorhombic). The present work is concerned with the existence of polymorphic forms of both the sodium and potassium salts. The cubic forms of NaCN and KCN exhibit polymorphic transitions to orthorhombic structures at temperatures of 288.3 and 163.1 K respectively. The enthalpies of transition are known[1]. We calculate the total lattice potential energy of the two forms in each case and a knowledge of the enthalpy of transition enables us to fix the charge distribution and also the lattice energy for these salts. The dipole moment of the  $\text{CN}^-$  ion is calculated and values are assigned for  $\Delta H_f^\circ(\text{CN}^-(g))$  and  $\Delta H_{\text{ion}}^\circ(\text{CN}^-(g))$ , for the proton affinity of the gaseous cyanide ion corresponding to the process:



and for the electron affinity of the gaseous cyanide radical.

On the basis of the above values we assign lattice energies for other cyanides using the Born-Haber cycle.

While several studies exist for the cubic salts (Sherman[2], Yatsimirskii[3, 4], Waddington[5], Ladd and Lee[6], Morris[7] and Ladd[8]) only one previous study exists for the orthorhombic salts (Ladd[8]).

## CALCULATIONS

At room temperature NaCN and KCN have the cubic NaCl arrangement with free rotation of the  $\text{CN}^-$  ions and cell lengths  $a = 5.893 \text{ \AA}$  for NaCN and  $a = 6.527 \text{ \AA}$  for KCN. At lower temperatures this rotation cannot be maintained and the structures both resort to orthorhombic symmetry: NaCN having a bimolecular unit cell with dimensions[9-12]  $a = 3.774 \text{ \AA}$ ,  $b = 4.719 \text{ \AA}$ ,  $c = 5.64 \text{ \AA}$  and KCN having a bimolecular unit cell with dimensions[9, 10, 13-17]  $a = 4.24 \text{ \AA}$ ,  $b = 5.14 \text{ \AA}$ ,  $c = 6.17 \text{ \AA}$ .

In the orthorhombic case a distributed charge is chosen to reside on the atoms of the  $\text{CN}^-$  ion, a charge  $q_c$  on the carbon atom and a charge  $q_n$  on the nitrogen atom, in such a way that:

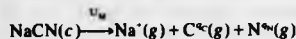
$$q_c + q_n = -1. \quad (1)$$

### (i) Total lattice potential energies

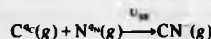
The total lattice potential energies of the two polymorphs were calculated using the "term-by-term" equation:

$$U_{\text{pot}} = U_M + U_{\text{SE}} + U_D - U_R \quad (2)$$

Where the electrostatic components,  $U_M$  and  $U_{\text{SE}}$ , are the electrostatic energies of the processes:



and



and  $U_D$  and  $U_R$  are the dispersion and repulsion energies.

The Madelung constants,  $M$  and associated energies,  $U_M$ , were calculated, in the orthorhombic case, using the Bertaut method[18]. The results, given in Table 1, take the form:

$$M = \sum_{i=1}^{\infty} \alpha_i \cdot q_N^i \quad (3)$$

$$U_M = \sum_{i=1}^{\infty} A_i \cdot q_N^i. \quad (4)$$

We can also express the Madelung constant as a parameter based on unit distance ( $A(L)/L$  in Ladd's notation[8]):

$$\frac{M}{L} = \sum_{i=1}^{\infty} \left( \frac{\alpha_i}{L} \right) \cdot q_N^i = \frac{A(L)}{L} \quad (5)$$

and generate specifically:

$$\frac{M(\text{NaCN})}{L} = 0.6013 + 0.9924 \cdot q_N + 0.9924 \cdot q_N^2 \quad (6)$$

$$\frac{M(\text{KCN})}{L} = 0.5465 + 0.9576 \cdot q_N + 0.9576 \cdot q_N^2. \quad (7)$$

As we have pointed out previously[19] these equations mirror the Ladd[8] results for individual charges quoted in

Table 1. Calculation of total lattice potential energies of cubic and orthorhombic forms of NaCN and KCN

		NaCN		KCN		Notes
		Cubic	Orthorhombic	Cubic	Orthorhombic	
M	$a_0$	0.593098	0.629972	0.535488	0.589937	based on CN distance $L$ or $a$ as indicated
	$a_1$	—	1.039965	—	1.033728	
	$a_2$	—	1.039965	—	1.033728	
	$L$	—	1.0476	—	1.0794	A
	$a_{MCN}$	5.893	—	6.527	—	A
$U_M$	$A_0$	824.0	835.4	744.0	759.3	kJ mol <sup>-1</sup>
	$A_1$	—	1379.2	—	1330.5	kJ mol <sup>-1</sup>
	$A_2$	—	1379.2	—	1330.5	kJ mol <sup>-1</sup>
$U_{SE}$	$B_1$	—	-1326.1	—	-1287.1	kJ mol <sup>-1</sup>
	$B_2$	—	-1326.1	—	-1287.1	kJ mol <sup>-1</sup>
	$C_0$	824.0	835.4	744.0	759.3	kJ mol <sup>-1</sup>
$U_{ELEC}$	$C_1$	—	53.1	—	43.4	kJ mol <sup>-1</sup>
	$C_2$	—	53.1	—	43.4	kJ mol <sup>-1</sup>
$U_R$	$r_+$	0.875	0.875	1.185	1.185	A
	$\bar{r}$	1.57	1.23	1.57	1.23	A
	$U_R$	100.5	96.8	88.6	93.4	kJ mol <sup>-1</sup>
	$\epsilon$	82.55	82.55	45.84	45.84	ergs molecule <sup>-1</sup>
	$\epsilon$	5.625	5.625	5.625	5.625	ergs molecule <sup>-1</sup>
$U_D$	$\alpha$	0.182	0.182	0.844	0.844	A'
	$\alpha$	2.80	2.80	2.80	2.80	A'
	$U_D$	5.4	6.0	8.4	9.8	kJ mol <sup>-1</sup>
	$D_0$	728.9	744.6	663.8	675.7	kJ mol <sup>-1</sup>
	$D_1$	—	53.1	—	43.4	kJ mol <sup>-1</sup>
$U_{TOT}$	$D_2$	—	53.1	—	43.4	kJ mol <sup>-1</sup>

his paper, but are Madelung energies and therefore do not take into account the self energies of the ions.

The Madelung constants and energies for the cubic forms of NaCN and KCN are calculated directly from the Madelung constant for NaCl ( $=1.747565$ , based on  $L=1$  unit cell length) using the cell lengths of the cubic structures,  $a_{MCN}$ , quoted in the first paragraph of this section and the equation:

$$M(MCN) = \frac{2M_{NaCl}}{a_{MCN}} \quad (8)$$

For the self energies of the ions:

$$U_{SE} = \sum_{i=1}^2 B_i \cdot q_N^i \quad (9)$$

In the orthorhombic case  $U_{SE}$  was calculated explicitly but in the cubic salts, where the  $CN^-$  ion is considered as a point charge ion freely rotating, no self energy term was required. The results are quoted in Table 1. Thus for the orthorhombic salts the total electrostatic energy,  $U_{ELEC}$ , is given by:

$$U_{ELEC} = A_0 + \sum_{i=1}^2 (A_i + B_i) \cdot q_N^i = \sum_{i=0}^2 C_i q_N^i \quad (10)$$

whereas for the cubic salts, we take:

$$U_{ELEC} = U_M \quad (11)$$

The repulsion energies,  $U_R$ , are calculated by the method of Huggins and Mayer[20] from the equations:

$$U_R = U_R^{++} + U_R^{+-} + U_R^{--} \quad (12)$$

where:

$$U_R^{++} = \frac{bc_{++}}{2} \cdot \exp\left(\frac{2F_+}{\rho}\right) \sum_{i=1}^{M+N} \exp(-R_{M+N}/\rho) \quad (13)$$

in both the orthorhombic and cubic cases, and:

$$U_R^{+-} = \frac{bc_{+-}}{2} \cdot \exp\left(\frac{2F_-}{\rho}\right) \times \left[ \sum_{i=1}^{M+N} \exp(-R_{CN}/\rho) + \sum_{i=1}^{M+N} \exp(-R_{CN}/\rho) \right] \quad (14)$$

in the orthorhombic case, and:

$$U_R^{--} = \frac{bc_{--}}{2} \cdot \exp\left(\frac{2F_-}{\rho}\right) \cdot \sum_{i=1}^{M+N} \exp(-R_{CN}/\rho) \quad (15)$$

in the cubic case, where  $R_{CN_{int}}$  is the internal C-N bond length in the  $CN^-$  ion and  $R_{CN_{ext}}$  is the CN-CN ion distance, when the  $CN^-$  ions are considered as point charge ions.

$$U_R^{+-} = bc_{+-} \cdot \exp\left(\frac{F_+ + F_-}{\rho}\right) \left[ \sum_{i=1}^{M+N} \exp(-R_{M+N}/\rho) + \sum_{i=1}^{M+N} \exp(-R_{M+N}/\rho) \right] \quad (16)$$

for the orthorhombic case, and:

$$U_R^{--} = bc_{--} \cdot \exp\left(\frac{F_+ + F_-}{\rho}\right) \cdot \sum_{i=1}^{M+N} \exp(-R_{M+N}/\rho) \quad (17)$$

for the cubic case.

$R_{MCN}$  is the distance from the cation to the centroid of the  $CN^-$  ion treated as a point charge. In all the above cases  $F_+$  is the Huggins "basic" radius of the  $M^+$  ion. In the orthorhombic case the  $CN^-$  ion was treated in the form of a model of two separate atoms each considered to have a radius of 1.23 Å ( $F_-$ ) (the value for oxygen) on the basis of

$$= \frac{1}{2} \epsilon_+ \alpha_+ S_6^{++} + \frac{1}{2} \epsilon_- \alpha_- S_6^{--} + \frac{1}{4} \frac{\epsilon_+ \epsilon_- \alpha_+ \alpha_-}{(\epsilon_+ + \epsilon_-)} S_6^{+-}$$
$$S_6^{++} = \sum_{M=1}^{M-M} (1/R_{M-M})^6 \quad (20)$$
$$S_6^{--} = \frac{1}{2} \left\{ \sum_{C=C}^{C=C} (1/R_{C-C})^6 + \sum_{N=N}^{N=N} (1/R_{N-N})^6 \right\} \quad (21)$$
$$S_6^{--} = \sum^{CN-CN} (1/R_{CN-CNi})^6 \quad (22)$$
$$S_6^{-1} = \frac{1}{2} \left\{ \sum_{i=1}^{M-C} (1/R_{M-C_i})^6 + \sum_{i=1}^{M-N} (1/R_{M-N_i})^6 \right\} \quad (23)$$
$$S_6^{+-} = \sum_i^{M, CN} (1/R_{M, CNi})^6 \quad (24)$$
$$U_{\text{POT}} = \sum_{i=1}^N D_i q_N^i \quad (25)$$

Since (Fig. 1) the total lattice potential energy is determined, for the orthorhombic salts, as a function of the distributed charge on the CN<sup>-</sup> ion, we must use the known enthalpies of transition (cubic to orthorhombic) in order to estimate the precise lattice energies.

Table 2. Literature values for lattice energies of NaCN and KCN and thermodynamic parameters for the gaseous CN<sup>-</sup> ion[illegible]

Term by term method

term by term method.

††Lyotropic number value.

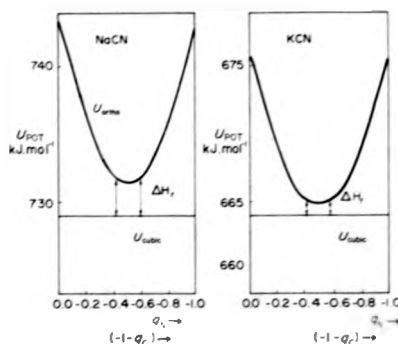
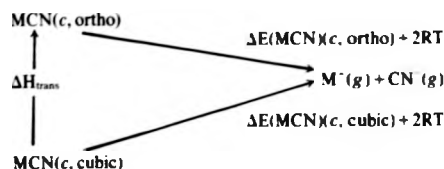


Fig. 1.

From the cycle:



we know  $\Delta H_{\text{trans}}$  (experimentally)  $\Delta H_{\text{trans}} = -2.93 \text{ kJ mol}^{-1}$  at 288.3 K for NaCN and  $\Delta H_{\text{trans}} = -1.26 \text{ kJ mol}^{-1}$  at 168.1 K for KCN. We can equate the enthalpy terms to give:

$$\Delta H_{\text{trans}} = \Delta E(\text{MCN})(c, \text{cubic}) - \Delta E(\text{MCN})(c, \text{ortho}) \quad (26)$$

where the right hand side refers to the total internal energy changes in going from the crystal to the gaseous ions respectively for the cubic and orthorhombic salts. We can easily show that:

$$U_{\text{POT}}(\text{MCN}) = \Delta E(\text{MCN})(c) + 2RT \quad (27)$$

and so we can directly equate  $\Delta H_{\text{trans}}$  to the lattice potential energy difference between the two salts.

$$\Delta H_{\text{trans}} = U_{\text{POT}}(\text{MCN})(\text{cubic}) - U_{\text{POT}}(\text{MCN})(\text{ortho}). \quad (28)$$

Thus in Fig. 1, when the gap between the  $U_{\text{POT}}(\text{MCN})(\text{cubic})$  line and the  $U_{\text{POT}}(\text{MCN})(\text{ortho})$  curve attains the

value  $\Delta H_{\text{trans}}$ , we can assume that the corresponding ordinate values give the lattice potential energies of the salts.

These considerations generate the values:

$$U_{\text{POT}}(\text{NaCN})(\text{ortho}) = 731.7 \text{ kJ mol}^{-1} \quad (29)$$

$$U_{\text{POT}}(\text{NaCN})(\text{cubic}) = 728.8 \text{ kJ mol}^{-1} \quad (30)$$

$$U_{\text{POT}}(\text{KCN})(\text{ortho}) = 665.1 \text{ kJ mol}^{-1} \quad (31)$$

$$U_{\text{POT}}(\text{KCN})(\text{cubic}) = 663.8 \text{ kJ mol}^{-1} \quad (32)$$

and we compare the results with other work in Table 2.

(ii) Estimation of the charge distribution in the  $\text{CN}^-$  ion

A feature of the crystal structures, the inverse relation of the carbon and nitrogen atoms to one another, ensures that:

$$U_{\text{POT}} = \sum_i D_i q_i = \sum_j D_j q_j \quad (33)$$

and hence the abscissae in Fig. 1 can be interpreted as either  $q_C$  or  $q_N$  values. Consistent with the quantum mechanical estimates of the  $\text{CN}^-$  ion charges and with simple electronegativity arguments we assign from the NaCN results, values:

$$q_C = -0.42 \quad \text{and} \quad q_N = -0.58 \quad (34)$$

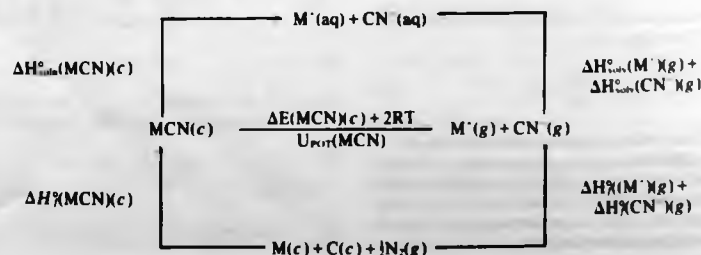
and from the KCN results:

$$q_C = -0.43 \quad \text{and} \quad q_N = -0.57. \quad (35)$$

These results can be compared to the quantum mechanical calculations for the  $\text{CN}^-$  ion of Demnynck *et al.* [24] ( $q_C = -0.43$ ,  $q_N = -0.57$ ) and of Hillier and Saunders [25] ( $q_C = -0.41$ ,  $q_N = -0.59$ ) but differ from the assignment of Ladd [8] of charges ( $q_C(q_N) = -0.05$ ,  $q_N(q_C) = -0.95$ ). The dipole moment of the  $\text{CN}^-$  ion has received some attention by theoreticians. Bonaccorsi, Petrongolo *et al.* [26] have calculated  $\mu(\text{CN}^-)$  to be 0.81 D while their earlier calculations [27] suggest  $\mu(\text{CN}^-)$  to be 1.84 D. Ladd [8] reports on the basis of his charges, a value of 2.40 D. Our value for the charges give a dipole moment of the order 0.4 D, but the actual value is a matter of speculation not fact.

(iii) Thermodynamic parameters for the gaseous  $\text{CN}^-$  ion

Consideration of the cycle:



we can assume that the corresponding values give the lattice potential energies of the

considerations generate the values:

$$U_{\text{pot}}(\text{NaCN})(\text{ortho}) = 731.7 \text{ kJ mol}^{-1} \quad (29)$$

$$U_{\text{pot}}(\text{NaCN})(\text{cubic}) = 728.8 \text{ kJ mol}^{-1} \quad (30)$$

$$U_{\text{pot}}(\text{KCN})(\text{ortho}) = 665.1 \text{ kJ mol}^{-1} \quad (31)$$

$$U_{\text{pot}}(\text{KCN})(\text{cubic}) = 663.8 \text{ kJ mol}^{-1} \quad (32)$$

compare the results with other work in Table 2.

tion of the charge distribution in the  $\text{CN}^-$  ion of the crystal structures, the inverse relation of and nitrogen atoms to one another, ensures that:

$$U_{\text{pot}} = \sum_{i=1}^n D_i q_i' = \sum_{i=1}^n D_i q_i' \quad (33)$$

the abscissae in Fig. 1 can be interpreted as or  $q_N$  values. Consistent with the quantum estimates of the  $\text{CN}^-$  ion charges and with electronegativity arguments we assign from the ults, values:

$$q_C = -0.42 \text{ and } q_N = -0.58 \quad (34)$$

the KCN results:

$$q_C = -0.43 \text{ and } q_N = -0.57. \quad (35)$$

results can be compared to the quantum mechanical calculations for the  $\text{CN}^-$  ion of Demnyck *et al.* [24] (3,  $q_N = -0.57$ ) and of Hillier and Saunders [25] (1,  $q_N = -0.59$ ) but differ from the assignment of  $f$  charges ( $q_C(q_N) = -0.05$ ,  $q_N(q_C) = -0.95$ ). The ment of the  $\text{CN}^-$  ion has received some attention ticians. Bonaccorsi, Petrongolo *et al.* [26] have  $\mu(\text{CN}^-)$  to be 0.81 D while their earlier ns [27] suggest  $\mu(\text{CN}^-)$  to be 1.84 D. Ladd [8] the basis of his charges, a value of 2.40 D. Our the charges give a dipole moment of the order the actual value is a matter of speculation not

odynamic parameters for the gaseous  $\text{CN}^-$  ion eration of the cycle:

$$\Delta H_{\text{ion}}^{\circ}(\text{M}^+(g)) + \Delta H_{\text{ion}}^{\circ}(\text{CN}^-(g))$$



$$\Delta H^{\circ}(\text{M}^+(g)) + \Delta H^{\circ}(\text{CN}^-(g))$$

leads us to equations:

$$\Delta H^{\circ}(\text{CN}^-(g)) = U_{\text{pot}}(\text{MCN}) + \Delta H^{\circ}(\text{MCN})(c) - \Delta H^{\circ}(\text{M}^+(g)) \quad (36)$$

and:

$$\Delta H_{\text{ion}}^{\circ}(\text{CN}^-(g)) = \Delta H_{\text{ion}}^{\circ}(\text{MCN})(c) - U_{\text{pot}}(\text{MCN}) - \Delta H_{\text{ion}}^{\circ}(\text{M}^+(g)). \quad (37)$$

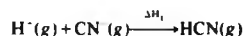
Using the known values [28] of  $\Delta H^{\circ}(\text{NaCN})(c, \text{cubic}) = -89.8 \text{ kJ mol}^{-1}$ ,  $\Delta H^{\circ}(\text{KCN})(c, \text{cubic}) = -112.6 \text{ kJ mol}^{-1}$ ,  $\Delta H^{\circ}(\text{Na}^+(g)) = 609.8 \text{ kJ mol}^{-1}$ ,  $\Delta H^{\circ}(\text{K}^+(g)) = 514.2 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{ion}}^{\circ}(\text{NaCN})(c, \text{cubic}) = 1.26 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{ion}}^{\circ}(\text{KCN})(c, \text{cubic}) = 11.71 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{ion}}^{\circ}(\text{Na}^+(g)) = -405.9 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{ion}}^{\circ}(\text{K}^+(g)) = -321.9 \text{ kJ mol}^{-1}$ . We find using eqn (36) the value  $\Delta H^{\circ}(\text{CN}^-(g)) = 29.2 \text{ kJ mol}^{-1}$  from the sodium salt data and the value  $\Delta H^{\circ}(\text{CN}^-(g)) = 37.1 \text{ kJ mol}^{-1}$  from the potassium salt data. Accordingly we assign an average value:

$$\Delta H^{\circ}(\text{CN}^-(g)) = 33 \text{ kJ mol}^{-1}. \quad (38)$$

Using eqn (37) we find from the sodium salt data  $\Delta H_{\text{ion}}^{\circ}(\text{CN}^-(g)) = -321.7 \text{ kJ mol}^{-1}$  and from the potassium salt data  $\Delta H_{\text{ion}}^{\circ}(\text{CN}^-(g)) = -330.2 \text{ kJ mol}^{-1}$  and accordingly assign:

$$\Delta H_{\text{ion}}^{\circ}(\text{CN}^-(g)) = -326 \text{ kJ mol}^{-1}. \quad (39)$$

Using the above data for the  $\text{CN}^-$  ion we can calculate the proton affinity of the gaseous  $\text{CN}^-$  ion, i.e. the enthalpy change of the process:



The proton affinity,  $\Delta H_1$ , is given by:

$$\Delta H_1 = \Delta H^{\circ}(\text{HCN}(g)) - \Delta H^{\circ}(\text{H}^+(g)) - \Delta H^{\circ}(\text{CN}^-(g)) \quad (40)$$

and since the thermochemical values  $\Delta H^{\circ}(\text{HCN}(g)) = 135.1 \text{ kJ mol}^{-1}$  and  $\Delta H^{\circ}(\text{H}^+(g)) = 1536.20 \text{ kJ mol}^{-1}$  are known [29], then using the value of  $\Delta H^{\circ}(\text{CN}^-(g))$  we have assigned we can estimate  $\Delta H_1$ . We obtain the result:

$$\Delta H_1 = -1434 \text{ kJ mol}^{-1}. \quad (41)$$

This value should be compared to the theoretically calculated values (the  $\Delta E$  values calculated have been corrected to give enthalpy values) of Hopkinson *et al.* [30], who obtain:  $\Delta H_1 = -2889 \text{ kJ mol}^{-1}$  (using a minimum (31/1) basis set);  $\Delta H_1 = -1639 \text{ kJ mol}^{-1}$  (using a medium (52/2) basis set);  $\Delta H_1 = -1470 \text{ kJ mol}^{-1}$  (using a large (73/3) basis set) and  $\Delta H_1 = -1915 \text{ kJ mol}^{-1}$  (at the Hartree Fock limit).

Their best calculation, using the large Gaussian basis set, agrees fairly well with our value, as it does with the "experimental" value of  $-1412 \text{ kJ mol}^{-1}$  they quote. The source of this latter value is obscure since an incorrect reference is cited. More recently Bonaccorsi *et al.* [26] have performed a double zeta-SCFMOLCAO calculation and obtained a value for  $\Delta H_1 = -1554 \text{ kJ mol}^{-1}$  (corrected  $\Delta E$  value) which compares well to their "experimental" value,  $\Delta H_1 = -1538 \text{ kJ mol}^{-1}$ , but not as well to our  $\Delta H_1$  value or to the "experimental" value of Hopkinson *et al.*

We can also use our data for the gaseous  $\text{CN}^-$  ion to estimate the electron affinity of the cyanide radical.



From the above we can deduce:

$$\text{EA}(\text{CN}^-) - 5/2 \cdot \text{RT} = \Delta H^{\circ}(\text{CN}^-(g)) - \Delta H^{\circ}(\text{CN}^{\cdot}(g)). \quad (42)$$

Now  $\Delta H^{\circ}(\text{CN}^{\cdot}(g)) = 441.4 \text{ kJ mol}^{-1}$  [32] and so:

$$\text{EA}(\text{CN}^-) = -402 \text{ kJ mol}^{-1} = -4.2 \text{ eV}. \quad (43)$$

This value can be compared to other literature values. Moore [33], in an NBS circular, quotes a value of 3.2 eV which Herron and Dibler [34] agreed with in their electron impact studies of CNCl, CNBr and CNI. Bakulina and Ionov [35] reported a value of 3.7 eV by measuring the difference between the electron affinities of sulphur atoms and cyanide radicals. Berkowitz, Chupka and Walter [32], by photoionisation of HCN, quote a value of 3.8 eV. Comparing our value to those above it would appear that our heat of formation of the  $\text{CN}^-$  ion may be too low, leading to a high figure for our electron affinity of the cyanide radical and the proton affinity of the  $\text{CN}^-$  ion.

(iv) Estimation of the lattice energies of other cyanide salts

From a Born-Haber cycle we find, for a cyanide of a divalent metal,  $\text{M}(\text{CN})_2$ :

$$U_{\text{pot}}(\text{M}(\text{CN})_2) = \Delta H^{\circ}(\text{M}^{2+}(g)) + 2\Delta H^{\circ}(\text{CN}^-(g)) - \Delta H^{\circ}(\text{M}(\text{CN})_2)(c) - 7/2 \cdot \text{RT} \quad (44)$$

and for the monovalent metal cyanides,  $\text{MCN}$ :

$$U_{\text{pot}}(\text{MCN}) = \Delta H^{\circ}(\text{M}^+(g)) + \Delta H^{\circ}(\text{CN}^-(g)) - \Delta H^{\circ}(\text{MCN})(c). \quad (45)$$

Using the value of  $\Delta H^{\circ}(\text{CN}^-(g))$  estimated in our study we can, using the known values [29] for  $\Delta H^{\circ}(\text{M}(\text{CN})_2)(c)$ ,  $\Delta H^{\circ}(\text{MCN})(c)$ ,  $\Delta H^{\circ}(\text{M}^{2+}(g))$  and  $\Delta H^{\circ}(\text{M}^+(g))$ , estimate the lattice energies of other cyanide salts. The results are given in Table 3 and compared, where available, to other literature estimates.

A similar equation:

$$U_{\text{pot}} = \Delta H_{\text{ion}}^{\circ}(\text{M}(\text{CN})_2)(c) - \Delta H_{\text{ion}}^{\circ}(\text{M}^{2+}(g)) - \Delta H_{\text{ion}}^{\circ}(\text{CN}^-(g)) - 7/2 \cdot \text{RT} \quad (46)$$

in conjunction with known [29] solution data, can be used to estimate the lattice energies of these salts. The results are combined in Table 3.

## DISCUSSION

The value for  $\Delta H^{\circ}(\text{CN}^-(g))$  lies within the wide range covered by other determinations of the parameter (Table 2), while the value for  $\Delta H_{\text{ion}}^{\circ}(\text{CN}^-(g))$  shows broad agreement with the two previously cited values (Table 2). The lattice energies of NaCN are in excellent agreement with Ladd's values [8] although the figures for KCN differ appreciably from his. The cubic results lie in the middle of the range covered by other literature values.

An independent study is in progress to obtain further values for all the above parameters, but the current



Table 3. Comparison of projected values of lattice energies of some cyanide salts using thermodynamic data derived in this paper, with literature values

Salt	(All values in $\text{kJ mol}^{-1}$ )					Ladd and Lee (1960)		Yatsimirskii (1961)	
	Enthalpy of formation of cryst. salt	Enthalpy of formation of gas. cation	Enthalpy of solution of cryst. salt	Enthalpy of solution of gas. cation	$U_{\text{calc.}}$ from eqn (44) & (45)	$U_{\text{calc.}}$ from eqn (46)	Ref. [6]	Ref. [4]	Ref. [36]
$\text{Cd}(\text{CN})_2$	162.3	2623.5	—	—	2519	—	2548	—	2284 2619 2611
$\text{Hg}(\text{CN})_2$	263.6	2990.4	—	—	2684	—	2715	—	2226 2782 2661
$\text{Pd}(\text{CN})_2$	238.1	3069.4	—	—	2889	—	—	—	—
$\text{Zn}(\text{CN})_2$	95.8	2782.7	—	—	2744	—	2791	—	2431 2891 2891
$\text{Cu}(\text{CN})_2$	-184.5	1925.9	-53.68	-1567.4*	2168	2157.2	2213	2268	—
$\text{Ba}(\text{CN})_2$	-218.4	1660.5	-11.7†	-1360.7*	1936	1992.4	2004	2046	—
$\text{CaCN}$	96.2	1090.0	—	—	1027	—	—	—	—
$\text{AgCN}$	146.0	1019.2	—	—	906	—	925	—	741 954

\*Kapustin &amp; Yatsimirskii equation; †Born Haber cycle.

‡Estimated from  $\Delta H_f^\circ(\text{M}(\text{CN})_2, \text{aq}) - \Delta H_f^\circ(\text{M}(\text{CN})_2, \text{cr})$ .†Taken from Lister, Halliwell and Nyburg [31];  $\Delta H_f^\circ(\text{M}^+, \text{aq}) - \Delta H_f^\circ(\text{M}^+, \text{cr}) + 2\Delta H_{\text{sub}}^\circ(\text{H}^+, \text{aq})$ .

estimates give the lattice energies of the other salts in reasonably close agreement to the values obtained by Ladd and Lee[6]. We shall reconsider the overall values of  $\Delta H^{\circ}(\text{CN})^-(g)$  and  $\Delta H^{\circ}_{\text{tot}}(\text{CN})^-(g)$  on completion of our further studies.

## REFERENCES

1. C. E. Messer and W. T. Ziegler, *J. Am. Chem. Soc.* **63**, 2703 (1941).
2. J. Sherman, *Chem. Revs.* **11**, 93 (1932).
3. K. B. Yatsimirskii, *Izvest. Akad. Nauk. SSSR, Otdel Khim. Nauk*, p. 453, (1947).
4. K. B. Yatsimirskii, *J. Gen. Chem.* **26**, 2655 (1956).
5. T. C. Waddington, *Adv. Inorg. Chem. Radiochem.* **1**, 159 (1959).
6. M. F. C. Ladd and W. H. Lee, *J. Inorg. Nucl. Chem.* **14**, 14 (1960).
7. D. F. C. Morris, *Acta. Cryst.* **14**, 547 (1961).
8. M. F. C. Ladd, *Trans. Faraday Soc.* **65**, 2712 (1969).
9. R. W. G. Wyckoff, *Crystal Structures*, 2nd. Edn. Interscience, New York (1964).
10. G. Natta and L. Passerini, *Gazz. Chim. Ital.* **61**, 191 (1931).
11. H. J. Verweel and J. M. Bijvoet, *Z. Krist.* **100A**, 201 (1938).
12. L. A. Siegel, *J. Chem. Phys.* **17**, 1146 (1949).
13. P. A. Cooper, *Nature* **107**, 745 (1921).
14. R. M. Bozorth, *J. Am. Chem. Soc.* **44**, 317 (1922).
15. P. A. Cooper, *Nature* **110**, 544 (1922).
16. J. M. Bijvoet and J. A. Lely, *Rec. Trav. Chim.* **59**, 908 (1940).
17. N. Elliott and J. Hastings, *Acta. Cryst.* **14**, 1018 (1961).
18. E. F. Bertaut, *J. Phys. Radium* **13**, 499 (1952).
19. H. D. B. Jenkins and T. C. Waddington, *Nature Phys. Sci.* **228**, 126 (1972).
20. M. L. Huggins and J. E. Meyer, *J. Chem. Phys.* **1**, 643 (1933).
21. F. London, *Z. Physik. Chem. (Leipzig)* **B11**, 222 (1930).
22. M. F. C. Ladd and W. H. Lee, *Prog. Solid State Chem.* **1**, 37 (1964).
23. J. R. Tessman, A. H. Kahn and W. Shockley, *Phys. Rev.* **92**, 890 (1953).
24. J. Demnynck, A. Veillard and G. Vinot, *Chem. Phys. Lett.* **10**, 522 (1971).
25. I. H. Hillier and V. R. Saunders, *Mol. Phys.* **23**, 449 (1972).
26. R. Bonaccorsi, C. Petrongolo, E. Scrocco and J. Tomasi, *Chem. Phys. Lett.* **3**, 473 (1969).
27. R. Bonaccorsi, C. Petrongolo, E. Scrocco and J. Tomasi, *J. Chem. Phys.* **48**, 1500 (1968).
28. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of chemical thermodynamic properties*, NBS Circular 500, Natl. Bur. Stands., U.S. Govt. Printing Office, Washington (1952).
29. V. B. Parker, D. D. Wagman and W. H. Evans, *Selected Values of Chemical Thermodynamic Properties*, NBS Tech. Note 270-1, U.S. Dept. of Commerce, NBS, Washington DC (1971).
30. A. C. Hopkinson, N. K. Holbrook, K. Yates and I. G. Csizmedia, *J. Chem. Phys.* **49**, 3596 (1968).
31. M. W. Lister, S. C. Nyburg and R. B. Poyntz, *J. Chem. Soc. (Faraday I)* **70**, 684 (1974).
32. J. Berkowitz, W. A. Chupka and T. A. Walter, *J. Chem. Phys.* **50**, 1497 (1969).
33. C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467, U.S. Govt. Printing Office, Washington (1952).
34. J. T. Herron and V. H. Dibler, *J. Am. Chem. Soc.* **82**, 1555 (1960).
35. I. N. Bakulina and N. I. Ionov, *Russian J. Phys. Chem. (Eng. transl.)*, **33**, 286 (1959).
36. K. B. Yatsimirskii, *Zhur. Neorg. Khim.* **6**, 518 (1961).



## LATTICE POTENTIAL ENERGIES OF ORTHORHOMBIC AND CUBIC CYANIDES OF THE ALKALI METALS

ENTHALPY OF FORMATION,  $\Delta H_f^\circ(\text{CN}^-)(g)$  AND SOLVATION,  $\Delta H_{\text{solv}}^\circ(\text{CN}^-)(g)$  OF GASEOUS CYANIDE ION. EXPERIMENTAL DETERMINATION OF THE ENTHALPY OF SOLUTION OF CRYSTALLINE LITHIUM CYANIDE,  $\Delta H_{\text{soln}}^\circ(\text{LiCN})(c)$ , PROTON AFFINITY OF CYANIDE ION AND ELECTRON AFFINITY OF  $\text{CN}^\cdot$  RADICAL

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**Abstract**—The lattice energies of the cubic and orthorhombic forms of the alkali metal cyanides are calculated:  $U_{\text{pot}}(\text{LiCN})_{\text{ortho}} = 828 \text{ kJ mol}^{-1}$ ,  $U_{\text{pot}}(\text{NaCN})_{\text{ortho}} = 736 \text{ kJ mol}^{-1}$ ,  $U_{\text{pot}}(\text{NaCN})_{\text{cubic}} = 729 \text{ kJ mol}^{-1}$ ,  $U_{\text{pot}}(\text{KCN})_{\text{ortho}} = 669 \text{ kJ mol}^{-1}$ ,  $U_{\text{pot}}(\text{KCN})_{\text{cubic}} = 664 \text{ kJ mol}^{-1}$ ,  $U_{\text{pot}}(\text{RbCN})_{\text{cubic}} = 638 \text{ kJ mol}^{-1}$  and  $U_{\text{pot}}(\text{CsCN})_{\text{cubic}} = 601 \text{ kJ mol}^{-1}$ . Using these results we estimate  $\Delta H_f^\circ(\text{CN}^-)(g) = 36 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{solv}}^\circ(\text{CN}^-)(g) = -329 \text{ kJ mol}^{-1}$ , the proton affinity of the gaseous  $\text{CN}^-$  ion to be  $-1438 \text{ kJ mol}^{-1}$ , the dipole moment to be  $\mu(\text{CN}^-) = 1.62 \text{ D}$  and the electron affinity of the cyanide radical to be  $-380$  or  $-399 \text{ kJ mol}^{-1}$  depending on the value of  $\Delta H_f^\circ(\text{CN}^-)(g)$  used.

### INTRODUCTION

The alkali metal cyanides are cubic at room temperature with the exception of LiCN, which is orthorhombic. The cubic forms of NaCN and KCN exhibit polymorphic transitions to orthorhombic structures at temperatures of 288.3 and 168.1 K respectively. Lattice energies have been determined mainly for the cubic crystals but recent studies by Ladd[1] and by Jenkins and Pratt[2] have considered the orthorhombic salts. The results of Sherman[3], Yatsimskii[4, 5], Waddington[6], Ladd and Lee[7], Morris[8] and Ladd[1] are given in Table 1, from which can be seen the wide divergence of results obtained. These results lead in turn to wide discrepancies in other thermodynamic parameters such as the enthalpy of formation of the gaseous cyanide ion,  $\Delta H_f^\circ(\text{CN}^-)(g)$  and its enthalpy of solvation,  $\Delta H_{\text{solv}}^\circ(\text{CN}^-)(g)$  as can be seen in Table 2. The present work attempts to calculate the total lattice potential energies for all the alkali metal cyanides, to assign thermodynamic parameters for the  $\text{CN}^-$  ion and to consider the charge distribution in the ion.

### CALCULATIONS

At room temperature NaCN and KCN have the cubic NaCl arrangement with free rotation of the  $\text{CN}^-$  ions and cell lengths, for NaCN  $a = 5.893 \text{ \AA}$ , and for KCN  $a = 6.527 \text{ \AA}$ , at lower temperatures this rotation cannot be maintained and the structures resort to orthorhombic symmetries[9].

Orthorhombic NaCN[9, 11, 12, 13] has a bimolecular unit cell with parameters  $a = 3.774 \text{ \AA}$ ,  $b = 4.719 \text{ \AA}$  and  $c = 5.64 \text{ \AA}$  and KCN[9, 11, 14-17] has a bimolecular unit cell with parameters  $a = 4.24 \text{ \AA}$ ,  $b = 5.14 \text{ \AA}$  and  $c = 6.17 \text{ \AA}$ .

The orthorhombic LiCN[9, 10] has a tetramolecular cell with parameters  $a = 3.73 \text{ \AA}$ ,  $b = 6.52 \text{ \AA}$ ,  $c = 8.73 \text{ \AA}$ .

RbCN[9, 11] is a cubic cell with NaCl arrangement with

$a = 6.82 \text{ \AA}$  and CsCN[9, 11] has the CsCl arrangement with  $a = 4.25 \text{ \AA}$ .

A distributed charge is chosen to reside on the atoms of the  $\text{CN}^-$  ion. A charge  $q_C$  is placed on the carbon atom and a charge  $q_N$  on the nitrogen such that:

$$q_C + q_N = -1. \quad (1)$$

#### (i) The total lattice potential energies

The "term by term" expression for the total lattice potential energy takes the form:

$$U_{\text{pot}}(\text{MCN}) = U_M + U_{\text{SE}} + U_D - U_R \quad (2)$$

where  $U_M$  is the Madelung component of the electrostatic energy and  $U_{\text{SE}}$  is the internal electrostatic energy of the  $\text{CN}^-$  ions,  $U_D$  is the dispersion energy and  $U_R$  is the repulsion energy.

The calculation of  $U_{\text{SE}}$ , the combination of  $U_M$  and  $U_{\text{SE}}$ , proceeds for the orthorhombic salts as follows. The Madelung constants,  $M$ , and energies,  $U_M$ , were calculated for each structure using the Bertaut method[19]. The results take the form:

$$M = \sum_{i=1}^{\infty} \alpha_i q_N^i \quad (3)$$

$$U_M = \sum_{i=1}^{\infty} A_i q_N^i \quad (4)$$

where  $\alpha_i$  and  $A_i$  are the usual coefficients expressing the charge dependence, the values are cited in Table 3.

For the self energies of the ions:

$$U_{\text{SE}} = \sum_{i=1}^{\infty} B_i q_N^i \quad (5)$$

Table 1. The lattice energies of alkali metal cyanides ( $\text{kJ mol}^{-1}$ )

Lattice Energies, $U_{\text{pot}}$ ( $\text{kJ mol}^{-1}$ )	1932 Shannon [3] (a)	1947 Yates [4] (b)	1956 Yates [5] (b)	1959 Haddad [6] (c)	1960 Ladd [7] (a)	1961 Morris [8] (f)	1969 Ladd [1] (e)	1975 Jenkins/Pratt [2] (d)	1975 This work (d)
LiCN orthorhombic	-	803	-	-	-	-	791	-	828
KCN orthorhombic	-	-	-	-	-	-	734	732	736
RbCN cubic	709	769	774	728	712	761	728	729	729
ECN orthorhombic	-	-	-	-	-	-	677	665	669
ECN cubic	648	678	699	663	655	665	676	664	664
BCN cubic	624	648	674	632	629	-	640	-	638
CCN cubic	591	623	644	582	596	-	611	-	601

(a) Born-Landé equation. (b) Yates [4] Equation (c) Born-Mayer Equation (d) Term by Term (e) Ladd and Lee Equation  
(f) Lyscopic number determination.

Table 2. Enthalpy data for gaseous cyanide ion ( $\text{kJ mol}^{-1}$ )

Source	$\Delta H_f^\circ(\text{CN}^-)(\text{g})$	$\Delta H_{\text{solv}}^\circ(\text{CN}^-)(\text{g})$	Notes
Sherman [3] 1932	23.1	-	average
Yatsimirskii [4] 1947	53.8	-	average
Yatsimirskii [5] 1956	71.1	-	
Waddington [6] 1959	29.9 28.0	- -	average average
Ladd and Lee [7] 1960	54.4	- 305	
Morris [8] 1961	46.0	-	
Ladd [1] 1969	$44.3 \pm 4$	- $285 \pm 4$	
Berkowitz, Chupka and Watter [31] 1969	68.5	-	experimental
Jenkins and Pratt [2] 1975	33	- 326	
This work 1975	36	- 329	

Table 3. Computational results for orthorhombic cyanides

Parameter	LiCN	NaCN	KCN	Notes
M	$\sigma_0$ 0.676302 $\sigma_1$ 0.881748 $\sigma_2$ 1.009264 $L/\text{\AA}$ 1.1421	0.629972 1.039965 1.039965 1.0476	0.589937 1.033728 1.033728 1.0794	based on C-N shortest distances = L
$U_{\text{Li}}$ kJ mol <sup>-1</sup>	A <sub>0</sub> 822.7 A <sub>1</sub> 1072.6 A <sub>2</sub> 1227.7	835.4 1379.2 1379.2	759.3 1330.5 1330.5	
$U_{\text{SE}}$ kJ mol <sup>-1</sup>	B <sub>1</sub> -1216.4 B <sub>2</sub> -1216.4	-1326.1 -1326.1	-1287.1 -1287.1	
$U_{\text{elec}}$ kJ mol <sup>-1</sup>	C <sub>0</sub> 822.7 C <sub>1</sub> -143.8 C <sub>2</sub> 11.3	835.5 53.0 53.0	759.3 43.4 43.4	
$U_{\text{R}}$ kJ mol <sup>-1</sup>	$U_{\text{R}}^{++}$ 0.5 $U_{\text{R}}^{+-}$ 14.9 $U_{\text{R}}^{-+}$ 107.4 $U_{\text{R}}^{--}$ 122.8	0.4 12.6 83.8 96.8	0.7 3.8 88.9 93.4	
$U_{\text{D}}$ kJ mol <sup>-1</sup>	$U_{\text{D}}^{++}$ 0.0 $U_{\text{D}}^{+-}$ 3.5 $U_{\text{D}}^{-+}$ 1.0 $U_{\text{D}}^{--}$ 4.5	0.2 3.0 2.9 6.0	1.2 1.6 7.0 9.8	
$U_{\text{pot}}$ kJ mol <sup>-1</sup>	D <sub>0</sub> 704.4 D <sub>1</sub> -143.8 D <sub>2</sub> 11.3	744.6 53.0 53.0	675.7 43.4 43.4	

where the  $B_i$  coefficients express the self energy term charge dependence.

In the orthorhombic case  $U_{se}$  was calculated explicitly and the results are listed in Table 3. In the cubic phases, since the CN<sup>-</sup> ions are rotating, the rest of the lattice "sees" these ions as spheres of charge distribution and  $U_M = U_{elec}$ .

The electrostatic contribution,  $U_{elec}$  is therefore calculated. The repulsion energies of the salts are calculated using the equations given

$$U_{elec} = \sum_{i=1}^N C q_N^i \quad (6)$$

in Ref. [2], which employ the Huggins and Mayer method[20]. The dispersion energies are calculated from the London[21] formula as given in Ref. [2]. The results for  $U_R$  and  $U_D$  are given in Tables 3 and 4. The total lattice potential energies are then calculated.

$$U_{pot} = \sum_{i=1}^N D q_N^i \quad (7)$$

On the basis of the charge distributions ( $q_N = -0.81$ ) calculated later we find the total lattice potential energies of the alkali metal cyanides to be:

$$U_{pot}(\text{LiCN})_{ortho} = 828.3 \text{ kJ mol}^{-1}$$

$$U_{pot}(\text{NaCN})_{ortho} = 736.4 \text{ kJ mol}^{-1}$$

$$U_{pot}(\text{KCN})_{ortho} = 669.0 \text{ kJ mol}^{-1}$$

$$U_{pot}(\text{NaCN})_{cubic} = 728.8 \text{ kJ mol}^{-1}$$

$$U_{pot}(\text{KCN})_{cubic} = 663.8 \text{ kJ mol}^{-1}$$

$$U_{pot}(\text{RbCN})_{cubic} = 638.4 \text{ kJ mol}^{-1}$$

$$U_{pot}(\text{CsCN})_{cubic} = 600.9 \text{ kJ mol}^{-1}$$

The results above are compared to our recent estimates (in the case of NaCN and KCN) and to other calculations in the literature in Table 1.

(ii) *Enthalpy of formation of CN<sup>-</sup> ion,  $\Delta H_f^\circ(\text{CN}^-)(g)$*

In order to carry out this study it was necessary to prepare a sample of LiCN and then measure  $\Delta H_{sol}^\circ(\text{LiCN})(c)$  experimentally. The preparation and subsequent measurement are described in the Experimental Section of this paper. The results obtained were that  $\Delta H_{sol}^\circ(\text{LiCN})(c) = -6.5 \text{ kJ mol}^{-1}$ . Combining the known values of  $\Delta H_f^\circ(\text{Li}^+)(aq) = -278.4 \text{ kJ mol}^{-1}$ [22] and  $\Delta H_f^\circ(\text{CN}^-)(aq) = 150.62 \text{ kJ mol}^{-1}$ [23] with the above result gives a value of  $\Delta H_f^\circ(\text{LiCN})(c) = -121.3 \text{ kJ mol}^{-1}$ . Values for the sodium and potassium salts are available. From the cycle:

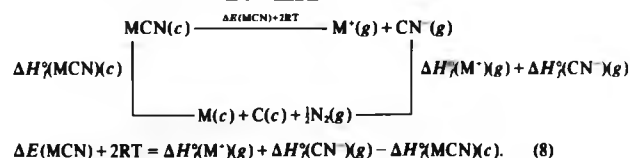


Table 4. Computational results for cubic cyanides

Parameter		NaCN	KCN	RbCN	CsCN
	$L_{\text{MCN}} \text{ \AA}$	2.946	3.263	3.41	4.25
$U_M = U_{elec}$ $\text{kJ mol}^{-1}$	$U_M / \text{kJ mol}^{-1}$	824.0	744.0	712.0	665.4
$U_R$ $\text{kJ mol}^{-1}$	$U_R^{++}$	0.4	0.7	0.8	4.7
	$U_R^{+-}$	14.3	3.9	2.1	5.7
	$U_R^{--}$	85.9	84.0	81.3	73.1
	$U_R$	100.5	88.6	84.2	83.4
$U_D$ $\text{kJ mol}^{-1}$	$U_D^{++}$	0.2	1.1	2.1	6.9
	$U_D^{+-}$	2.8	1.5	1.1	1.4
	$U_D^{--}$	2.4	5.8	7.4	10.5
	$U_D$	5.4	8.4	10.6	18.9
$U_{pot}$ $\text{kJ mol}^{-1}$	$D_0$	728.8	663.8	638.4	600.9
	$D_1$	0.0	0.0	0.0	0.0
	$D_2$	0.0	0.0	0.0	0.0

$$U_{\text{pot}}(\text{NaCN})_{\text{ortho}} = 736.4 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{KCN})_{\text{ortho}} = 669.0 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{NaCN})_{\text{cubic}} = 728.8 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{KCN})_{\text{cubic}} = 663.8 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{RbCN})_{\text{cubic}} = 638.4 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{CsCN})_{\text{cubic}} = 600.9 \text{ kJ mol}^{-1}$$

Its above are compared to our recent estimates of NaCN and KCN) and to other calculations in Table 1.

py of formation of  $\text{CN}^-$  ion,  $\Delta H_f^\circ(\text{CN}^-)(g)$  to carry out this study it was necessary to sample of LiCN and then measure  $N(c)$  experimentally. The preparation and measurement are described in the Experiment of this paper. The results obtained were that  $N(c) = -6.5 \text{ kJ mol}^{-1}$ . Combining the known  $\Delta H_f^\circ(\text{Li}^+)(aq) = -278.4 \text{ kJ mol}^{-1}$  [22] and  $(aq) = 150.62 \text{ kJ mol}^{-1}$  [23] with the above result of  $\Delta H_f^\circ(\text{LiCN})(c) = -121.3 \text{ kJ mol}^{-1}$ . Values of lithium and potassium salts are available. From the

Simple thermodynamic arguments show that the total internal energy change,  $\Delta E(\text{MCN}) + 2RT$  can be equated to the total lattice potential energy of the salt:

$$\Delta E(\text{MCN}) + 2RT = U_{\text{pot}}(\text{MCN}) \quad (9)$$

and hence

$$\Delta H_f^\circ(\text{CN}^-)(g) = U_{\text{pot}}(\text{MCN})(c) + \Delta H_f^\circ(\text{MCN})(c) - \Delta H_f^\circ(\text{M}^+)(g) \quad (10)$$

We use the known values  $\Delta H_f^\circ(\text{NaCN})(c, \text{cubic}) = -89.79 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{NaCN})(c, \text{orthorhombic}) = -92.72 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{KCN})(c, \text{cubic}) = -112.55 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{KCN})(c, \text{orthorhombic}) = -113.81 \text{ kJ mol}^{-1}$  [22, 24] and  $\Delta H_f^\circ(\text{Li}^+)(g) = 687.16 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{Na}^+)(g) = 609.84 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{K}^+)(g) = 514.2 \text{ kJ mol}^{-1}$ .

From the data for LiCN we find (in  $\text{kJ mol}^{-1}$ )

$$\Delta H_f^\circ(\text{CN}^-)(g) = -104.06 - 143.80q_N + 11.27q_N^2 \quad (11)$$

from that for NaCN, for the cubic case we find:

$$\Delta H_f^\circ(\text{CN}^-)(g) = 29.19 \text{ kJ mol}^{-1} \quad (12)$$

and for the orthorhombic salt

$$\Delta H_f^\circ(\text{CN}^-)(g) = 42.08 + 53.02q_N + 53.02q_N^2 \quad (13)$$

for KCN, the orthorhombic case gives:

$$\Delta H_f^\circ(\text{CN}^-)(g) = 47.7 + 43.41q_N + 43.41q_N^2 \quad (14)$$

and for the cubic case:

$$\Delta H_f^\circ(\text{CN}^-)(g) = 37.06 \text{ kJ mol}^{-1} \quad (15)$$

The curves (11) to (15) are plotted in Fig. 1. Table 5 gives details of the intersection points and values:

$$\Delta H_f^\circ(\text{CN}^-)(g) = 36.35 \text{ kJ mol}^{-1} \quad (16)$$

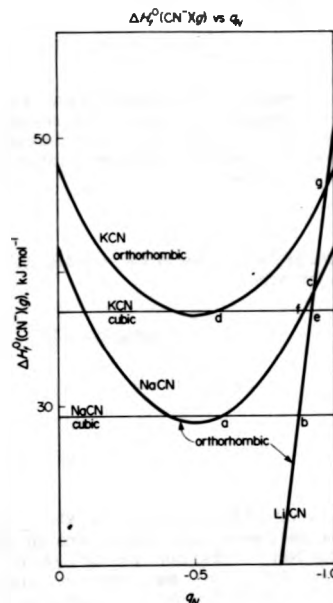


Fig. 1.

Table 5. Intersection points in Fig. 1.  $\Delta H_f^\circ(\text{CN}^-)(g)$  vs  $q_N$

Point	$\Delta H_f^\circ(\text{CN}^-)(g)$ (kJ mol <sup>-1</sup> )	$q_N$ (proton units)
a	29.19	-0.58
b	29.19	-0.87
c	38.33	-0.92
d	37.06	-0.57
e	37.06	-0.92
f	37.06	-0.86
g	46.57	-0.97
Overall average	36.35	-0.81
Average of c and g	42.45	-0.94

Intersection Points in Figure 2.  $\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g)$  vs  $q_N$

Point	$\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g)$ (kJ mol <sup>-1</sup> )	$q_N$ (proton units)
a	-321.70	-0.58
b	-321.70	-0.85
c	-330.04	-0.91
d	-330.17	-0.57
e	-330.17	-0.91
f	-330.17	-0.86
g	-339.16	-0.96
Overall Average	-329.02	-0.81
Average of c and g	-334.60	-0.94

ic cyanides

	RbCN	CsCN
	3.41	4.25
	712.0	665.4
	0.8	4.7
	2.1	5.7
	81.3	73.1
	84.2	83.4
	2.1	6.9
	1.1	1.4
	7.4	10.5
	10.6	18.9
	638.4	600.9
	0.0	0.0
	0.0	0.0

$$q_N = -0.81 \quad (17)$$

are assigned.

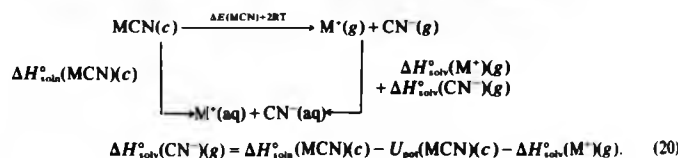
As has been noted in our earlier study [2], the symmetry of lattice potential energy curves for which

$$U_{\text{pot}} = \sum_{i=0}^3 D_i q_N^i = \sum_{i=0}^3 D_i q_C^i \quad (18)$$

means that abscissae for intersection points to the right of  $q_N = -0.5$  correspond to  $q_N$  charges while abscissae for intersection points to the left of  $q_N = -0.5$  correspond to  $q_C$  values and are related to the former abscissae by the required relationship:

$$q_C + q_N = -1. \quad (19)$$

(iii) *Enthalpy and solvation of  $\text{CN}^-$  ion*,  $\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g)$   
From the cycle:



Using the value  $\Delta H_{\text{sol}}^\circ(\text{LiCN})(c) = -6.5 \text{ kJ mol}^{-1}$  determined in this present study, together with the values  $\Delta H_{\text{sol}}^\circ(\text{NaCN})(c) = 1.26 \text{ kJ mol}^{-1}$  and  $\Delta H_{\text{sol}}^\circ(\text{KCN})(c) = 11.71 \text{ kJ mol}^{-1}$  [22] and the solvation energies:  $\Delta H_{\text{sol}}^\circ(\text{Li}^+)(g) = -520.25 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{sol}}^\circ(\text{Na}^+)(g) = -405.86 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{sol}}^\circ(\text{K}^+)(g) = -321.93 \text{ kJ mol}^{-1}$ , taken from Halliwell and Nyberg [25] we obtain the equations below.

From the orthorhombic salts, the data for LiCN gives:

$$\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g) = -190.65 + 143.80q_N - 11.27q_N^2 \quad (21)$$

for NaCN we have:

$$\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g) = -334.59 - 53.02q_N - 53.02q_N^2 \quad (22)$$

and for KCN we have:

$$\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g) = -340.81 - 43.41q_N - 43.41q_N^2 \quad (23)$$

for the cubic data, for NaCN

$$\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g) = -321.70 \text{ kJ mol}^{-1} \quad (24)$$

and for KCN

$$\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g) = -330.17 \text{ kJ mol}^{-1}. \quad (25)$$

Curves (21)–(25) are plotted in Fig. 2. Table 5 gives details of the intersection points and values

$$\Delta H_{\text{sol}}^\circ(\text{CN}^-)(g) = -329.0 \text{ kJ mol}^{-1} \quad (26)$$

$$q_N = -0.81 \quad (27)$$

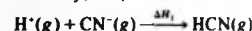
are assigned.

(iv) *Charge distribution in  $\text{CN}^-$  ion and dipole moment*

The value  $q_N = -0.81$ ,  $q_C = -0.19$  for the charge distribution of the  $\text{CN}^-$  ion is in reasonable agreement with the results of Demnynck, Veillard and Vinot [26] ( $q_N = -0.57$ ), Hillier and Sanders [27] ( $q_N = -0.59$ ) and of our earlier study [2] ( $q_N = -0.57$ ). The calculated dipole moment on the basis of a charge distribution as obtained in this study is found to be  $1.62D$  which lies between the values calculated recently by Bonaccorsi, Petrongolo, Scrocco and Tomasi [28, 29] ( $0.81D$ ,  $1.84D$ ).

(v) *Proton affinity of the  $\text{CN}^-$  ion*

The proton affinity,  $\Delta H_1$



for the gaseous cyanide ion, has received some attention in the literature and values (after correction for the RT term) of  $-1538 \text{ kJ mol}^{-1}$  [28],  $-1554 \text{ kJ mol}^{-1}$  [28],

$-1470 \text{ kJ mol}^{-1}$  [30] and  $-1434 \text{ kJ mol}^{-1}$  [2] have been assigned. Using the data [23]  $\Delta H_f^\circ(\text{HCN})(g) = 135.1 \text{ kJ mol}^{-1}$  and  $\Delta H_f^\circ(\text{H}^+)(g) = 1536.2 \text{ kJ mol}^{-1}$  we obtain from the present study, where  $\Delta H_f^\circ(\text{CN}^-)(g) = 36.4 \text{ kJ mol}^{-1}$ ,

$$\Delta H_1 = -1438 \text{ kJ mol}^{-1}. \quad (28)$$

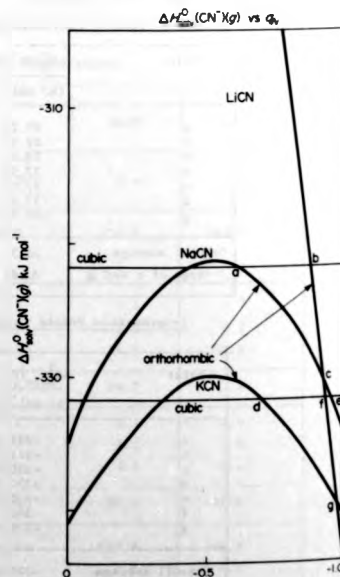
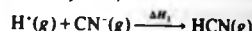


Fig. 2.

large distribution in  $\text{CN}^-$  ion and dipole moment value  $q_N = -0.81$ ,  $q_C = -0.19$  for the charge distribution of the  $\text{CN}^-$  ion is in reasonable agreement with results of Demynynck, Veillard and Vinot[26] (-0.57). Hillier and Sanders[27] ( $q_N = -0.59$ ) and of rlier study[2] ( $q_N = -0.57$ ). The calculated dipole moment on the basis of a charge distribution as obtained in this study is found to be 1.62D which lies between the calculated recently by Bonaccorsi, Petrongolo, and Tomasi[28, 29] (0.81D, 1.84D).

electron affinity of the  $\text{CN}^-$  ion  
proton affinity,  $\Delta H_1$



gaseous cyanide ion, has received some attention in literature and values (after correction for the RT of  $-1538 \text{ kJ mol}^{-1}$ [28],  $-1554 \text{ kJ mol}^{-1}$ [28],

$\text{CN}^-(g)$

$$\Delta H_{\text{ion}}^\circ(\text{M}^+)(g) + \Delta H_{\text{ion}}^\circ(\text{CN}^-)(g)$$

$$-U_{\text{ion}}(\text{MCN})(c) - \Delta H_{\text{ion}}^\circ(\text{M}^+)(g). \quad (20)$$

$1 \text{ kJ mol}^{-1}$ [30] and  $-1434 \text{ kJ mol}^{-1}$ [2] have been assumed. Using the data[23]  $\Delta H^\circ(\text{HCN})(g) = 135.1 \text{ kJ mol}^{-1}$   $\Delta H^\circ(\text{H}^+)(g) = 1536.2 \text{ kJ mol}^{-1}$  we obtain from the present study, where  $\Delta H^\circ(\text{CN}^-)(g) = 36.4 \text{ kJ mol}^{-1}$ ,

$$\Delta H_1 = -1438 \text{ kJ mol}^{-1}. \quad (28)$$

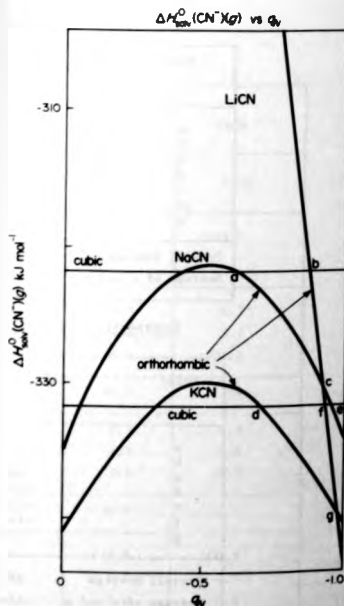


Fig. 2.

(vi) Electron affinity of  $\text{CN}^-$  radical

The electron affinity of the  $\text{CN}^-$  radical is given by the equation:

$$EA(\text{CN}^-) = \Delta H_f^\circ(\text{CN}^-(g)) - \Delta H_f^\circ(\text{CN}^\cdot(g)) - \frac{1}{2}RT. \quad (29)$$

Assuming our value for  $\Delta H_f^\circ(\text{CN}^\cdot(g))$  and using the values for  $\Delta H_f^\circ(\text{CN}^-(g))$  as indicated we obtain the results in Table 6 which can be compared to the literature values given there.

tatic charging of the particles was reduced by use of an American sample. (Found: C, 35.2, N, 42.9, Li, 20.9%. LiCN requires C, 36.4; N, 42.5; Li, 21.1%).

The enthalpy of solution was measured using the LKB 8700 Precision calorimeter system as manufactured by LKB Producter A.B. S-161 25 Bromma 1 Sweden, at Royal Holloway College, London. Several runs were made and it was a noticeable trend that values for  $\Delta H_{\text{sol}}^\circ(\text{LiCN})(c)$  as measured increased with time ( $-6.72 \text{ kJ mol}^{-1}$ ,  $-6.66 \text{ kJ mol}^{-1}$ ,  $-6.47 \text{ kJ mol}^{-1}$  and  $-6.21 \text{ kJ mol}^{-1}$ ) and we ascribed this trend to the fact that LiCN, being intensely hygroscopic, was picking up moisture even though

Table 6. Electron affinity and enthalpy of formation of  $\text{CN}^-$  radical

	$E(\text{CN}^\cdot)$	$\Delta H_f^\circ(\text{CN}^\cdot)(g)$
1932 Sherman [39]	3.0 eV	-
1932 Lederle [37]	4.0 eV <sup>a</sup>	-
1942 Rabinowitch [41]	3.0 eV <sup>a,c</sup>	-
1947 Matzner, Robertson and Chouk [38]	7.0 eV <sup>a</sup>	-
1953 Pritchard [40]	3.6 eV	-
1959 Stein and Tricinin [42]	3.0 eV <sup>a,c</sup>	-
1959 Bakulina and Ionov [33]	3.7 eV <sup>a</sup>	-
1960 Herroo and Dible [34]	3.2 eV <sup>a</sup>	-
1960-66 Janaf Tables [32]	3.9 eV	422.5 kJ mol <sup>-1</sup>
1961 Branscombe [43]	> 3.0 eV <sup>a</sup>	-
1962 Bulewicz and Padley [35]	3.0 eV <sup>a,c</sup>	-
1962 Bauer [36]	-	523 kJ mol <sup>-1</sup>
1963 Napper and Page [35]	2.8 eV <sup>a,c</sup>	387.9 kJ mol <sup>-1</sup>
1969 Berkowitz, Chupka and Walter [31]	3.8 eV <sup>a</sup> 4.2 eV <sup>b</sup>	441.4 kJ mol <sup>-1</sup>
1975 Jenkins and Pratt [2]	4.2 eV <sup>b</sup>	441.4 kJ mol <sup>-1</sup>
1975 This work	3.9 eV <sup>d</sup> 4.1 eV <sup>e</sup>	422.5 kJ mol <sup>-1</sup> 441.4 kJ mol <sup>-1</sup>

- Experimental values.
- Using present value for  $\Delta H_f^\circ(\text{CN}^\cdot)(g)$ .
- Based on Napper and Page's value for  $\Delta H_f^\circ(\text{CN}^\cdot)(g)$ [35], which is based on Cottrell's[44] value for  $\Delta H_f^\circ(\text{CN}^\cdot)(g)$ .
- Based on the  $\Delta H_f^\circ(\text{CN}^\cdot)(g)$  value in reference [32].
- Based on the  $\Delta H_f^\circ(\text{CN}^\cdot)(g)$  value in reference [23].

EXPERIMENTAL

The preparation of crystalline lithium cyanide was adapted from that of Perret and Perrot[45]. Small lumps of lithium metal were cut under petroleum ether and transferred to a glass ampule terminating in a RotaFlo TF6/24 tap. After evacuation a slight excess of anhydrous hydrogen cyanide was condensed onto the metal at 77 K. The mixture was carefully warmed towards room temperature until the reaction became vigorous when it was stopped by recooling to 77 K. The hydrogen was pumped away, further hydrogen cyanide added and the mixture again warmed towards room temperature. This process was repeated five times until a six-fold excess of hydrogen cyanide had been added. At this stage the reaction was not complete, but further reaction became very sluggish. The excess hydrogen cyanide was distilled from the mixture by pumping on it through a trap cooled to 77 K for 12 hr. The solid was transferred in a dry-box containing nitrogen dried with sodium-potassium alloy. The excess lithium metal was removed mechanically and the difficulty encountered with the transference of the very light powder due to the electro-

stringent precautions were taken at every stage to prevent this. An average value of  $-6.5 \text{ kJ mol}^{-1}$  was used for the present calculations.

DISCUSSION

The necessity of treating the  $\text{CN}^-$  ion as a spherical rotating charge in the cubic salts NaCN and KCN does not enable us to parameterise the cubic equations as charge dependent functions. Consequently values of the parameters in Table 5 derived from averages of the orthorhombic data (c and g) may be more reliable. The previous results[2] obtained from a consideration of the polymorphic modifications of NaCN and KCN and the known enthalpy of transition agree extremely well with those resulting from these studies. The thermodynamic data so derived (although somewhat at variance with the previous estimates (Table 2), particularly in the case of  $\Delta H_{\text{ion}}^\circ(\text{CN}^-)(g)$ ) we believe represent reasonable estimates of the parameters involved. We also must bear in mind that even the more comprehensive of all the previous studies (probably those of Ladd and Lee[1] and Morris[8]) do not use equations which are directly applicable to complex ions. In order to seek further validation

<sup>†</sup>This method produced a bulky white solid. If larger quantities of hydrogen cyanide are used to accelerate the reaction, higher temperatures and consequent polymerisation of the hydrogen cyanide occurs.



for the derived thermodynamic parameters for the gaseous  $\text{CN}^-$  ion we shall attempt to calculate  $\Delta H_f^\circ(\text{CN}^-(g))$  and other parameters from a study of the  $\text{NH}_4\text{CN}$  crystal, in addition to developing new approaches to the estimation of these quantities[46, 47].

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Dr C. J. Ludman is thanked for his perseverance in preparing a pure sample of LiCN when many proposed preparative schemes proved unsatisfactory. The assistance of M. Stephens Esq. with the practical work is acknowledged.

#### REFERENCES

1. M. F. C. Ladd, *Trans. Faraday Soc.* **65**, 2712 (1969).
2. H. D. B. Jenkins and K. F. Pratt, *J. Inorg. Nucl. Chem.* **38**, 1775 (1976).
3. J. Sherman, *Chem. Revs.* **11**, 93 (1932).
4. K. B. Yatsimirskii, *Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk* 453 (1947).
5. K. B. Yatsimirskii, *J. Gen. Chem.* **26**, 2655 (1956).
6. T. C. Waddington, *Adv. Inorg. Chem. Radiochem.* **1**, 159 (1959).
7. M. F. C. Ladd and W. H. Lee, *J. Inorg. Nucl. Chem.* **14**, 14 (1960).
8. D. F. C. Morris, *Acta Cryst.* **14**, 547 (1961).
9. R. W. G. Wyckoff, *Crystal Structures*, 2nd Edn. Interscience, New York (1964).
10. G. Natta and L. Passerini, *Gazz. Chim. Ital.* **61**, 191 (1931).
11. H. J. Verweel and J. M. Bijvoet, *Z. Krist.* **100A**, 201 (1938).
12. L. A. Siegel, *J. Chem. Phys.* **17**, 1146 (1949).
13. P. A. Cooper, *Nature* **107**, 745 (1921).
14. R. M. Bozorth, *J. Am. Chem. Soc.* **44**, 317 (1922).
15. P. A. Cooper, *Nature* **110**, 544 (1922).
16. J. M. Bijvoet and J. A. Lely, *Rec. Trav. Chim.* **59**, 908 (1940).
17. N. Elliott and J. Hastings, *Acta Cryst.* **14**, 1018 (1961).
18. H. D. B. Jenkins and T. C. Waddington, *Nature Phys. Sci.* **238**, 126 (1972).
19. E. F. Bertaut, *J. Phys. Radium* **13**, 499 (1952).
20. M. L. Huggins and J. E. Mayer, *J. Chem. Phys.* **1**, 643 (1933).
21. F. London, *Z. Physik. Chem. (Leipzig)* **B11**, 222 (1930).
22. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties* NBS Circular 500, Natl. Bur. Stands., U.S. Gov. Printing Office, Washington (1952).
23. V. B. Parker, D. D. Wagman and W. H. Evans, *Selected Values of Chemical Thermodynamic Properties*, NBS Tech. Note 270-1, U.S. Dept. of Commerce, N.B.S., Washington DC (1971).
24. C. E. Messer and W. T. Ziegler, *J. Am. Chem. Soc.* **63**, 2703 (1941).
25. H. F. Halliwell and S. C. Nyberg, *Trans. Faraday Soc.* **59**, 1126 (1963).
26. J. Demnynck, A. Veillard and G. Vinot, *Chem. Phys. Lett.* **10**, 522 (1971).
27. I. H. Hillier and V. R. Sanders, *Mol. Phys.* **23**, 449 (1972).
28. R. Bonaccorsi, C. Petrongolo, E. Scrocco and J. Tomasi, *Chem. Phys. Lett.* **3**, 473 (1967).
29. R. Bonaccorsi, C. Petrongolo, E. Scrocco and J. Tomasi, *J. Chem. Phys.* **40**, 1500 (1968).
30. A. C. Hopkinson, N. K. Holtbrook, K. Yates and I. G. Csizmedia, *J. Chem. Phys.* **49**, 3596 (1968).
31. J. Berkowitz, W. A. Chupka and T. A. Walter, *J. Chem. Phys.* **50**, 1497 (1969).
32. "Janaf" *Thermochemical Tables* (Edited by D. A. Stull), Dow Chemical Co. Midland, Michigan 1960-1966.
33. I. N. Bakulina and N. I. Ionov, *Russ. J. Phys. Chem.* **33**, 286 (1959).
34. J. T. Herron and V. H. Dibley, *J. Am. Chem. Soc.* **82**, 1555 (1960).
35. R. Napper and F. M. Page, *Trans. Faraday Soc.* **59**, 1086 (1963).
36. Wing Tsang, S. H. Bauer and M. Cowperthwaite, *J. Chem. Phys.* **36**, 1768 (1962).
37. E. Lederle, *Z. Physik. Chem. B*, **17**, 362 (1932).
38. F. A. Matsen, W. W. Robertson and R. L. Chouke, *Chem. Rev.* **41**, 273 (1947).
39. W. Sherman, *Chem. Rev.* **11**, 93 (1932).
40. H. O. Pritchard, *Chem. Rev.* **52**, 529 (1953).
41. E. Rabinowitch, *Rev. Mod. Phys.* **14**, 112 (1942).
42. G. Stein and A. Treinin, *Trans. Faraday Soc.* **55**, 1091 (1959).
43. L. Branscombe, *Proc. 5th Internat. Comb. Ionization Phenomena in Gases*, Vol. 1 (1961).
44. T. L. Cottrell, *The Strength of the Chemical Bond*, 2nd Edn. Butterworths, London (1958).
45. A. Perrot and R. Perrot, *Helv. Chim. Acta* **15**, 1165 (1932).
46. H. D. B. Jenkins and D. F. C. Morris, *Mol. Phys.* in press (1976).
47. H. D. B. Jenkins and K. F. Pratt, *J. Chem. Res.*, to be submitted (1977).



et al.

file, *Selected Values of Chemical Thermodynamic Properties* BS Circular 500, Natl. Bur. Stand., U.S. Gov. Printing Office, Washington (1952).

B. Parker, D. D. Wagman and W. H. Evans, *Selected values of Chemical Thermodynamic Properties*, NBS Tech. Note 270-1, U.S. Dept. of Commerce, N.B.S., Washington DC 971).

E. Messer and W. T. Ziegler, *J. Am. Chem. Soc.* **63**, 2703 (1941).

F. Halliwell and S. C. Nyberg, *Trans. Faraday Soc.* **59**, 126 (1963).

Demnynck, A. Veillard and G. Vinot, *Chem. Phys. Lett.* **10**, 22 (1971).

H. Hillier and V. R. Sanders, *Mol. Phys.* **23**, 449 (1972).

L. Bonaccorsi, C. Petrongolo, E. Scrocco and J. Tomasi, *Chem. Phys. Lett.* **3**, 473 (1967).

L. Bonaccorsi, C. Petrongolo, E. Scrocco and J. Tomasi, *J. Chem. Phys.* **48**, 1500 (1968).

A. C. Hopkinson, N. K. Holbrook, K. Yates and I. G. Sizmedia, *J. Chem. Phys.* **49**, 3596 (1968).

Berkowitz, W. A. Chupka and T. A. Walter, *J. Chem. Phys.* **40**, 1497 (1969).

'Janaf' *Thermochemical Tables* (Edited by D. A. Stull), Dow Chemical Co. Midland, Michigan 1960-1966.

N. Bakulina and N. I. Ionov, *Russ. J. Phys. Chem.* **33**, 286 (1959).

J. T. Herron and V. H. Dibley, *J. Am. Chem. Soc.* **82**, 1555 (1960).

R. Napper and F. M. Page, *Trans. Faraday Soc.* **59**, 1086 (1963).

Wing Tsang, S. H. Bauer and M. Cowperthwaite, *J. Chem. Phys.* **36**, 1768 (1962).

E. Lederle, *Z. Physik Chem. B*, **17**, 362 (1932).

F. A. Matsen, W. W. Robertson and R. L. Chouke, *Chem. Rev.* **41**, 273 (1947).

W. Sherman, *Chem. Rev.* **11**, 93 (1932).

H. O. Pritchard, *Chem. Rev.* **52**, 529 (1953).

E. Rabinowitch, *Rev. Mod. Phys.* **14**, 112 (1942).

G. Stein and A. Trieinin, *Trans. Faraday Soc.* **55**, 1091 (1959).

L. Branscombe, *Proc. 5th Internat. Comb. Ionisation Phenomena in Gases*, Vol. 1 (1961).

T. L. Cottrell, *The Strength of the Chemical Bond*, 2nd Edn. Butterworths, London (1958).

A. Perrot and R. Perrot, *Helv. Chim. Acta* **15**, 1165 (1932).

H. D. B. Jenkins and D. F. C. Morris, *Mol. Phys.* in press (1976).

H. D. B. Jenkins and K. F. Pratt, *J. Chem. Res.*, to be submitted (1977).

*Proc. R. Soc. Lond. A* **356**, 115-134 (1977)

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## On 'basic' radii of simple and complex ions and the repulsion energy of ionic crystals

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This paper proposes a method in which minimization criteria are employed, within the framework of the Huggins and Mayer method for the calculation of repulsion energy in ionic crystals, to establish 'basic' radii for both simple and complex spherical ions. With radii so generated repulsion energies (and hence total lattice energies) can be obtained for salts containing spherical ions. The paper initially establishes 'basic' radii for alkali metal and halide ions using more recent data than those used originally by Huggins. A description is then given of how we propose to employ the method for salts having spherical complex ions. The examples of potassium, rubidium, caesium, thallium and ammonium hexachloroplatinates are chosen and values for  $\Delta H_f^\circ(\text{PtCl}_6^{2-})(g)$  and  $\Delta H_{hyd}^\circ(\text{PtCl}_6^{2-})(g)$  are assigned on the basis of the repulsion, and hence the total lattice potential, energies calculated for these five salts.

Recent suspicions regarding the accuracy and reliability of the repulsion energy calculations for potassium hexachloroplatinate described in the current literature are re-examined and found to be justified.

### SYMBOLS

$A$	pre-exponential repulsion parameter
$a$	cubic lattice parameter
$A_0, A_p, B_p$	multipole expansion coefficients for Electrostatic Madelung parameter
$a_0$	value of cubic lattice parameter at energy minimum
$a_{CaF_2}$	value of lattice parameter in calcium fluoride
$\alpha_i, \alpha_j$	polarizabilities of ions $i$ and $j$
$b$	pre-exponential repulsion constant ( $= 10^{18} \text{ erg molecule}^{-1}$ )
$c_{++}, c_{--}, c_{+-}$	dipole-dipole dispersion energy pre summation factors (+, cation; -, anion)
$C_{++}, C_{--}, C_{+-}$	pre exponential repulsion factors (+, cation; -, anion)
$d$	internal distance in complex ion ( $= \text{Pt-Cl}$ )
$d_{++}, d_{--}, d_{+-}$	dipole-quadrupole dispersion energy pre summation factor (+, cation; -, anion)
$\eta_i, E_i, F_i$	charge induced coefficients in equations expressing $U_{elec}$ . $K(\partial M_{elec}/\partial a)_{a=a_0}$ and $\theta'_i$ as functions of $q_{Cl}$

$\Delta E$	total internal energy change for the 'lattice energy' step in the Born-Fajans-Haber cycle
$\overline{\Delta H}_{Cl}$	chloride ion affinity of crystalline $PtCl_2$ at 298.15 K and 1 atm pressure
$\Delta H_f^\circ(MX)(c)$	standard enthalpy of formation of compound MX in the crystalline state at 298.15 K and 1 atm pressure
$\Delta H_{hyd}^\circ(M^+)(g)$	standard enthalpy of hydration of the gaseous $M^+$ ion at 298.15 K and 1 atm pressure
$\Delta H_{soln}^\circ(MX)(c)$	standard enthalpy of solution of compound MX in the crystalline state at 298.15 K and 1 atm pressure
	electronic charge
$E_M, E_{PtCl_2}, E_{M,PtCl_2}$	total internal energy of $M^+$ , $PtCl_2^{2-}$ and $M_2PtCl_6$
$\epsilon_i, \epsilon_j$	characteristic energies of ions $i$ and $j$
$h, k, l$	indices describing unit cell
$h_P$	Planck's constant
$I_2$	second ionization potential ( $M^+ \rightarrow M^{2+}$ )
$k_{ij}$	distance parameter ( $= R_{ij}/a_0$ )
$K$	conversion factor ( $= 1389.30$ ) to convert units of $e^2 \text{ \AA}^{-1}$ to $\text{kJ mol}^{-1}$
$L$	integer index
$m$	mass of electron
$M_{elec}$	Electrostatic Madelung parameter
$n$	constant in Born-Landé equation
$\nu$	number of ions in stoichiometric unit
$p$	variable index in multipole expansion of $M_{elec}$
$p_i, p_j$	electron number of ions $i$ and $j$
$p_i(VE), p_i(HW)$	electron numbers derived from valence electron considerations and from Herzfeld & Woolf (1928) formula
$\phi_0, \phi_1, \phi_2, \phi_3$	rho dependent 'constants' relating charge on terminal atom of complex ion ( $q_A$ ) to the 'basic' radius
$q_i, q_j$	charge on ions $i$ and $j$
$q_{Cl}$	charge on terminal atom of complex ion
$Q_i, Q_j$	parameters for ions $i$ and $j$ defined by equation (18)
$\bar{r}_{M^+}, \bar{r}_{X^-}, \bar{r}_{PtCl_2^{2-}}$	'basic' radii of ions $M^+$ , $X^-$ and $PtCl_2^{2-}$
$R$	gas constant
$r_{nn}$	distance between nearest neighbour ions
$R_{MM}, R_{XX}, R_{MX}$	distance between reference $M^+$ , $X^-$ and $M^+$ ions and all other ions $M^+$ , $X^-$ and $X^-$ respectively, in the lattice
$R_{ij}$	distance between ions $i$ and $j$
$\rho$	repulsion constant
$S_i^{++}, S_i^{--}, S_i^{+-}$	dipole-dipole dispersion energy summations having inverse sixth power dependence (+, cation; -, anion)
$S_i^{++}, S_i^{--}, S_i^{+-}$	dipole-quadrupole dispersion energy summations having inverse eighth power dependence (+, cation; -, anion)

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pressure  
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of compound MX in the crystalline  
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of  $\text{M}^+$ ,  $\text{PtCl}_4^{2-}$  and  $\text{M}_2\text{PtCl}_6$   
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$\sum_{ij}$	general dispersion energy summation involving distance between $i$ th and $j$ th ion raised to $-L$ th power
$T$	absolute temperature
$\theta_1, \theta_2, \theta_3, \theta'_1, \theta'_2, \theta'_3$	calculable constants containing lattice repulsion summations specific to the individual $\text{M}_m\text{X}_n$ salt considered
$U_{\text{acou}}$	acoustic energy of the lattice
$U_{\text{elec}}$	electrostatic energy of the lattice
$U_{\text{dd}}$	dipole-dipole contribution to the dispersion energy of the lattice
$U_{\text{qd}}$	quadrupole-dipole contribution to the dispersion energy of the lattice
$U_r$	repulsion energy of the lattice
$U_{\text{pot}}$	total lattice potential energy of the lattice
$x_i, y_i, z_i$	fractional ion coordinates
$z^+, z^-$	charges on cation $\text{M}^{z+}$ and anion $\text{X}^{z-}$

## 1. INTRODUCTION

The condition that the lattice potential energy of a cubic crystalline lattice should be at an energy minimum leads to the equation:

$$\left(\frac{\partial U_r}{\partial a}\right)_{a=a_0} = \left(\frac{\partial U_{\text{elec}}}{\partial a}\right)_{a=a_0} + \left(\frac{\partial U_{\text{dd}}}{\partial a}\right)_{a=a_0} + \left(\frac{\partial U_{\text{qd}}}{\partial a}\right)_{a=a_0}, \quad (1)$$

where  $U_r$ ,  $U_{\text{elec}}$ ,  $U_{\text{dd}}$  and  $U_{\text{qd}}$  are the repulsion, electrostatic, dipole-dipole dispersion and quadrupole-dipole dispersion energy of the lattice and  $a$  is the lattice parameter.

By adopting a parametric form for  $U_r$  based on Huggins and Mayer's expression (Huggins & Mayer 1933; Huggins 1937; Mayer 1933) involving the 'basic' radii of the ions involved, the above equation leads, for a crystal  $\text{M}_m\text{X}_n$  to the expression:

$$\theta_1 \exp\left(\frac{2\bar{r}_{\text{M}^+}}{\rho}\right) + \theta_2 \exp\left(\frac{\bar{r}_{\text{M}^+} + \bar{r}_{\text{X}^-}}{\rho}\right) + \theta_3 \exp\left(\frac{2\bar{r}_{\text{X}^-}}{\rho}\right) = \frac{\left[U_{\text{elec}} + 6U_{\text{dd}} + 8U_{\text{qd}} - K\left(\frac{\partial M_{\text{elec}}}{\partial a}\right)_{a=a_0}\right]}{a_0}, \quad (2)$$

where  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  are calculable constants (based on individual lattice summations) and  $\bar{r}_{\text{M}^+}$ ,  $\bar{r}_{\text{X}^-}$  are the Huggins 'basic' radii of the ions  $\text{M}^{z+}$  and  $\text{X}^{z-}$ ,  $M_{\text{elec}}$  is the electrostatic Madelung constant of the lattice based on distance  $a_0$ , the cell constant. If we consider a general cubic lattice  $\text{M}_m\text{X}_n$  where the 'basic' radius,  $\bar{r}_{\text{M}^+}$  of the cation can be established, equation (2) then reduces to:

$$\theta_3 \exp(2\bar{r}_{\text{X}^-}/\rho) + \theta'_1 \exp(\bar{r}_{\text{X}^-}/\rho) + \theta'_1 = 0, \quad (3)$$

where

$$\theta'_1 = \theta_1 \exp(\bar{r}_{\text{M}^+}/\rho) \quad (4)$$

and

$$\theta'_1 = \theta_1 \exp\left(\frac{2\bar{r}_{\text{M}^+}}{\rho}\right) - \frac{\left[U_{\text{elec}} + 6U_{\text{dd}} + 8U_{\text{qd}} - K\left(\frac{\partial M_{\text{elec}}}{\partial a}\right)_{a=a_0}\right]}{a_0}, \quad (5)$$

(S)

or, alternatively, if the 'basic' radius of the anion is known, equation (2) reduces to

$$\theta_1 \exp(2\bar{r}_M/\rho) + \theta'_2 \exp(\bar{r}_M/\rho) + \theta'_3 = 0, \quad (6)$$

where

$$\theta'_2 = \theta_2 \exp(\bar{r}_X/\rho) \quad (7)$$

and

$$\theta'_3 = \theta_3 \exp\left(\frac{2\bar{r}_X}{\rho}\right) - \frac{\left[U_{elec} + 6U_{dd} + 8U_{qd} - K \left(\frac{\partial M_{elec}}{\partial a}\right)_{a=a_0}\right]}{a_0} \quad (8)$$

Equations (3) and (6) are solvable quadratic equations in  $\exp(\bar{r}_X/\rho)$  in the case of equation (3) and in  $\exp(\bar{r}_M/\rho)$  in the case of equation (6). If the ions  $X^{n-}$ , or  $M^{n+}$ , possess spherical symmetry, then the respective solutions of equations (3) and (6) assign a 'basic' radius to  $X^{n-}$ , or  $M^{n+}$ . Clearly there is no restriction on the complexity of the  $M^{n+}$  or  $X^{n-}$  ion except in so far that for the radius to have meaning the ion should be spherical.

## 2. THEORY

The lattice potential energy of an ionic solid is given by the term by term expression

$$U_{pot} = U_{elec} + U_{dd} + U_{qd} - U_r. \quad (9)$$

At equilibrium (corresponding to the lattice constant of the cubic structure,  $a$ , becoming equal to  $a_0$ ) the first derivative of the lattice potential energy with respect to this lattice constant is zero, giving

$$\left(\frac{\partial U_{pot}}{\partial a}\right)_{a=a_0} = \left(\frac{\partial U_{elec}}{\partial a}\right)_{a=a_0} + \left(\frac{\partial U_{dd}}{\partial a}\right)_{a=a_0} + \left(\frac{\partial U_{qd}}{\partial a}\right)_{a=a_0} - \left(\frac{\partial U_r}{\partial a}\right)_{a=a_0} = 0, \quad (10)$$

which generates equation (1).

When a specific form of these energy terms is taken we can obtain these first derivatives and substitute into equation (1). Thus, the electrostatic energy can be written:

$$U_{elec} = KM_{elec}/a_0, \quad (11)$$

where  $K$  is the conversion factor from  $e^2 \text{ \AA}^{-1}$  to  $\text{kJ mol}^{-1}$ . On differentiating we have

$$\left(\frac{\partial U_{elec}}{\partial a}\right)_{a=a_0} = \left[\frac{K}{a_0} \left(\frac{\partial M_{elec}}{\partial a}\right)_{a=a_0} - \frac{KM_{elec}}{a_0^2}\right]. \quad (12)$$

For a cubic lattice containing only monatomic ions (the case in the alkali halides,  $m = n = 1$ ),  $(\partial M_{elec}/\partial a)_{a=a_0}$  is zero and so:

$$\left(\frac{\partial U_{elec}}{\partial a}\right)_{a=a_0} = \left\{-\frac{U_{elec}}{a_0}\right\}. \quad (13)$$

The van der Waals dispersion terms  $U_{dd}$  and  $U_{qd}$  are given by

$$U_{dd} = \frac{1}{2}[c_{++}S_0^{++} + c_{--}S_0^{--}] + c_{+-}S_0^{+-}, \quad (14)$$

$$U_{qd} = \frac{1}{2}[d_{++}S_0^{++} + d_{--}S_0^{--}] + d_{+-}S_0^{+-}, \quad (15)$$

nion is known, equation (2) reduces to

$$(\bar{r}_{M^+}/\rho) + \theta'_s = 0, \quad (6)$$

$$\bar{r}_{X^-}/\rho \quad (7)$$

$$\frac{10 + 8U_{qd} - K \left( \frac{\partial M_{elec}}{\partial a} \right)_{a=a_0}}{a_0} \quad (8)$$

ic equations in  $\exp(\bar{r}_{X^-}/\rho)$  in the case of equation (6). If the ions  $X^{s-}$ , or  $M^{s+}$ , tive solutions of equations (3) and (6) here is no restriction on the complexity or the radius to have meaning the ion

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solid is given by the term by term  $+U_{qd} - U_r$ .

ice constant of the cubic structure,  $a$ , the lattice potential energy with respect

$$a_0 + \left( \frac{\partial U_{qd}}{\partial a} \right)_{a=a_0} - \left( \frac{\partial U_r}{\partial a} \right)_{a=a_0} = 0, \quad (10)$$

ms is taken we can obtain these first. Thus, the electrostatic energy can be

$$elec/a_0, \quad (11)$$

to  $\text{kJ mol}^{-1}$ . On differentiating we have

$$\left( \frac{\partial U_{elec}}{\partial a} \right)_{a=a_0} = - \frac{K M_{elec}}{a_0^2}. \quad (12)$$

mic ions (the case in the alkali halides,

$$\left( - \frac{U_{elec}}{a_0} \right). \quad (13)$$

nd  $U_{qd}$  are given by

$$S_0^{--}] + c_{+-} S_0^{+-}, \quad (14)$$

$$S_0^{--}] + d_{+-} S_0^{+-}, \quad (15)$$

where

$$c_{ij} = \frac{2e^4 Q_i Q_j}{3(\epsilon_i + \epsilon_j)}, \quad (16)$$

$$d_{ij} = \frac{3c_{ij}}{2} \left[ \frac{Q_i}{p_i} + \frac{Q_j}{p_j} \right], \quad (17)$$

$$Q_i = \frac{3\alpha_i \epsilon_i}{2e^3}. \quad (18)$$

$\alpha_i$ ,  $\epsilon_i$  and  $p_i$  are the polarizability, characteristic energy and electron number of the ion  $i$  and  $e$  is the electronic charge.

$$S_L^U = \sum_{all j} \left( \frac{1}{R_{ij}} \right)^L. \quad (19)$$

In these summations a reference ion  $i$  is taken, and the sum is over all  $j$  ions in the surrounding unit cells. For a cubic structure, the distance between a reference ion (fractional coordinates  $(x_j, y_j, z_j)$ ) and a general ion  $i$  (fractional coordinates  $(x_i, y_i, z_i)$ ) in a unit cell designated  $h, k, l$  is given by

$$R_{ij} = a\{(h+x_i-x_j)^2 + (k+y_i-y_j)^2 + (l+z_i-z_j)^2\}^{1/2} = ak_{ij}, \quad (20)$$

and therefore

$$\left( \frac{\partial S_L^U}{\partial a} \right)_{a=a_0} = - \sum_{all j} k_{ij}^L \left( \frac{1}{R_{ij}} \right)^{L+1} = - \frac{L S_L^U}{a_0}, \quad (21)$$

consequently

$$\left( \frac{\partial U_{dd}}{\partial a} \right)_{a=a_0} = - \frac{6 U_{dd}}{a_0} \quad (22)$$

and

$$\left( \frac{\partial U_{qd}}{\partial a} \right)_{a=a_0} = - \frac{8 U_{qd}}{a_0}. \quad (23)$$

In the case of salts of the type  $M_2PtCl_6$ , the summations  $S_L^U$  take the specific form

$$S_L^{M^+M^+} = 2 \left[ \sum_{\substack{all \text{ ions} \\ M^+}}^{M^+M^+} (R_{M^+M^+})^{-L} \right], \quad (24)$$

$$S_L^{M^+Cl^-} = 2 \left[ \sum_{\substack{all \text{ ions} \\ Cl^-}}^{M^+Cl^-} (R_{M^+Cl^-})^{-L} \right], \quad (25)$$

and

$$S_L^{Cl^-Cl^-} = 6 \left[ \sum_{\substack{all \text{ ions} \\ Cl^-}}^{Cl^-Cl^-} (R_{Cl^-Cl^-})^{-L} - 4(R_{Cl^-Cl_{\bar{a}}})^{-L} - (R_{Cl^-Cl_{\bar{a}\bar{a}}})^{-L} \right], \quad (26)$$

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where  $R_{\text{Cl-Cl}_i}$  and  $R_{\text{Cl-Cl}_{i+1}}$  are the chlorine-chlorine nearest neighbour and next nearest neighbour distances within the same  $\text{PtCl}_6^{2-}$  ion.

If we specifically consider an alkali halide crystal, MX, the repulsion energy is, following Huggins and Mayer, given by

$$U_r = \frac{1}{2}bC_{++} \exp\left(\frac{2\bar{r}_{M^+}}{\rho}\right) \sum_{\text{all } M_i} \exp\left(-\frac{R_{MM_i}}{\rho}\right) + \frac{1}{2}bC_{--} \exp\left(\frac{2\bar{r}_{X^-}}{\rho}\right) \sum_{\text{all } X_i} \exp\left(-\frac{R_{XX_i}}{\rho}\right) + bC_{+-} \exp\left(\frac{\bar{r}_{M^+} + \bar{r}_{X^-}}{\rho}\right) \sum_{\text{all } X_i} \exp\left(-\frac{R_{MX_i}}{\rho}\right), \quad (27)$$

where  $b$  is a constant ( $10^{12}$  erg molecule $^{-1}$ ) and

$$C_{ij} = \left(1 + \frac{q_i}{p_i} + \frac{q_j}{p_j}\right), \quad (28)$$

where  $q_i$  is the charge on the ion  $i$ ,  $\rho$  is a parameter, usually obtained from compressibility data. The summations are performed in a similar manner to those involved in the dispersion energy calculations. Using equation (27), and differentiating, we obtain

$$\left(\frac{\partial U_r}{\partial a}\right)_{a=a_0} = -\frac{1}{2}bC_{++} \exp\left(\frac{2\bar{r}_{M^+}}{\rho}\right) \sum_{\text{all } M_i} \left\{\left(\frac{k_{MM_i}}{\rho}\right) \exp\left(-\frac{R_{MM_i}}{\rho}\right)\right\} - \frac{1}{2}bC_{--} \exp\left(\frac{2\bar{r}_{X^-}}{\rho}\right) \sum_{\text{all } X_i} \left\{\left(\frac{k_{XX_i}}{\rho}\right) \exp\left(-\frac{R_{XX_i}}{\rho}\right)\right\} - bC_{+-} \exp\left(\frac{\bar{r}_{M^+} + \bar{r}_{X^-}}{\rho}\right) \sum_{\text{all } X_i} \left\{\left(\frac{k_{MX_i}}{\rho}\right) \exp\left(-\frac{R_{MX_i}}{\rho}\right)\right\}. \quad (29)$$

The summations involved in equation (29) can be computed in a similar manner to those defined earlier.

Substitution of equations (12), (22), (23) and (29) into equation (1) leads to an expression of the form of equation (2). Explicitly 20 equations can be produced for the alkali halides ( $m = n = 1$ ) where each  $\bar{r}_{M^+}$  appears in four equations and each  $\bar{r}_{X^-}$  in five. This set of equations cannot be solved directly, but provided we assign the 'basic' radius for one ion, all the 'basic' radii can be computed for all the other ions. The suitability, or otherwise, of the initial choice can be judged from the consistency found in the  $\bar{r}$  values for these other ions. The process may be continued in an iterative manner in order to deduce an optimum set of radii for the alkali metal and for the halide ions.

Other salts ( $m$  or  $n \neq 1$ ) like, for example,  $\text{M}_2\text{PtCl}_6$ , have slightly different expressions for their repulsion energies. Specifically, for an  $\text{M}_2\text{PtCl}_6$  salt having the

chlorine-chlorine nearest neighbour and next to same  $\text{PtCl}_6^{2-}$  ion.

halide crystal,  $\text{MX}$ , the repulsion energy is,  $y$

$$\frac{k_{\text{MM}_i}}{\rho} - \exp\left(\frac{2\bar{r}_{\text{X}^-}}{\rho}\right) \sum_{\text{all } \text{X}_i} \exp\left(-\frac{R_{\text{XX}_i}}{\rho}\right) - \exp\left(\frac{\bar{r}_{\text{M}^+} + \bar{r}_{\text{X}^-}}{\rho}\right) \sum_{\text{all } \text{X}_i} \exp\left(-\frac{R_{\text{MX}_i}}{\rho}\right), \quad (27)$$

$z^{-1}$ ) and

$$1 + \frac{q_i}{p_i} + \frac{q_i}{p_j}, \quad (28)$$

is a parameter, usually obtained from comparison performed in a similar manner to those calculations. Using equation (27), and differentiating

$$\left(\frac{k_{\text{MM}_i}}{\rho}\right) \exp\left(-\frac{R_{\text{MM}_i}}{\rho}\right) + \left(\frac{k_{\text{XX}_i}}{\rho}\right) \exp\left(-\frac{R_{\text{XX}_i}}{\rho}\right) + \frac{\bar{r}_{\text{M}^+} + \bar{r}_{\text{X}^-}}{\rho} \sum_{\text{all } \text{X}_i} \left(\frac{k_{\text{MX}_i}}{\rho}\right) \exp\left(-\frac{R_{\text{MX}_i}}{\rho}\right). \quad (29)$$

in (29) can be computed in a similar manner

(23) and (29) into equation (1) leads to an equation. Explicitly 20 equations can be produced for each  $\bar{r}_{\text{M}^+}$  appears in four equations and each can be solved directly, but provided we assign 'basic' radii can be computed for all the other ions. The initial choice can be judged from the results of other ions. The process may be continued until an optimum set of radii for the alkali metal

example,  $\text{M}_2\text{PtCl}_6$ , have slightly different radii. Specifically, for an  $\text{M}_2\text{PtCl}_6$  salt having the

antifluorite structure,  $U_r$  takes the form

$$U_r = \frac{1}{2} b C_{++} \exp\left(\frac{2\bar{r}_{\text{M}^+}}{\rho}\right) \left[ 2 \sum_{\text{all ions } \text{M}_i^+} \exp\left(-\frac{R_{\text{M}^+\text{M}_i^+}}{\rho}\right) + b C_{+-} \exp\left(\frac{\bar{r}_{\text{M}^+} + \bar{r}_{\text{PtCl}_6^{2-}}}{\rho}\right) \left[ 2 \sum_{\text{all ions } \text{PtCl}_6^{2-}} \exp\left(-\frac{R_{\text{M}^+\text{PtCl}_6^{2-}}}{\rho}\right) + \frac{1}{2} b C_{--} \exp\left(\frac{2\bar{r}_{\text{PtCl}_6^{2-}}}{\rho}\right) \left[ \sum_{\text{all ions } \text{PtCl}_6^{2-}} \exp\left(-\frac{R_{\text{PtCl}_6^{2-}\text{PtCl}_6^{2-}}}{\rho}\right) \right] \right] \right], \quad (30)$$

where  $\bar{r}_{\text{PtCl}_6^{2-}}$  is the 'basic' radius of the hexachloroplatinate ion. These expressions are still differentiable and the general equation (20) applies, and in the case above

$$\left(\frac{\partial U_r}{\partial a}\right)_{a=a_0} = -\frac{1}{2} b C_{++} \exp\left(\frac{2\bar{r}_{\text{M}^+}}{\rho}\right) \left[ 2 \sum_{\text{all ions } \text{M}_i^+} \left\{ \left(\frac{k_{\text{MM}_i}}{\rho}\right) \exp\left(-\frac{R_{\text{M}^+\text{M}_i^+}}{\rho}\right) \right\} - b C_{+-} \exp\left(\frac{\bar{r}_{\text{M}^+} + \bar{r}_{\text{PtCl}_6^{2-}}}{\rho}\right) \left[ 2 \sum_{\text{all ions } \text{PtCl}_6^{2-}} \left\{ \left(\frac{k_{\text{MPtCl}_6^{2-}}}{\rho}\right) \exp\left(-\frac{R_{\text{M}^+\text{PtCl}_6^{2-}}}{\rho}\right) \right\} - \frac{1}{2} b C_{--} \exp\left(\frac{2\bar{r}_{\text{PtCl}_6^{2-}}}{\rho}\right) \left[ \sum_{\text{all ions } \text{PtCl}_6^{2-}} \left\{ \left(\frac{k_{\text{PtCl}_6^{2-}\text{PtCl}_6^{2-}}}{\rho}\right) \exp\left(-\frac{R_{\text{PtCl}_6^{2-}\text{PtCl}_6^{2-}}}{\rho}\right) \right\} \right] \right] \right]. \quad (31)$$

In this paper we (i) establish the basic radii of the ions  $\text{M}^+$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$  and  $\text{Cs}$ ) and  $\text{X}^-$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ ) by consideration of 20 alkali metal salts as described; (ii) establish the basic radius of  $\text{Ti}^+$  and  $\text{NH}_4^+$  by considering  $\text{TiCl}$  and  $\text{NH}_4\text{Cl}$  by choosing the  $\bar{r}_{\text{Cl}^-}$  value determined above; and (iii) having obtained  $\bar{r}_{\text{M}^+}$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{Ti}$  and  $\text{NH}_4$ ), we consider  $\text{M}_2\text{PtCl}_6$  salts, to establish a basic radius for the  $\text{PtCl}_6^{2-}$  ion.

In this study a unique value is assumed for  $\rho$  for all the alkali halides, an approach often criticized, particularly (see Baughan 1959a, b; Tsai 1964) in the case where a single exponential term (rather than a sum of exponential terms, as in equation (27) for example), is used

$$U_r = A \exp(-r_{\text{nn}}/\rho), \quad (32)$$

where  $r_{\text{nn}}$  is the distance between nearest neighbours, for the parametric form of the repulsion energy. It must be recognized that in the present method admitting a variable  $\rho$  parameter introduces complications and, in the absence of compressibility data, makes repulsion energies difficult, if not impossible, to calculate within the Huggins and Mayer formulation. Assumption of a constant value for  $\rho$  is taken to be consistent with our previous work (Jenkins, Pratt, Smith & Waddington 1976; Jenkins & Pratt 1976a). We believe that in the particular method we are now proposing such errors that may be introduced by this assumption will be minimized since we are directly evaluating the basic radii, which themselves have a close parametric relationship to  $\rho$ .

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## 3. CALCULATIONS

In the case of the alkali halides, the cell constants used in this study are taken from Wyckoff (1965). The Madelung constants are well established. For the sodium chloride structure (structure type I)  $M_{elec}$  is 3.49513 (Waddington 1959) and for the caesium chloride structure (structure type II)  $M_{elec}$  is 2.035356 (Waddington 1959), both based on the cell constant  $a_0$  as the characteristic distance. The computation of  $U_{elec}$  is therefore straightforward.

The CsCl structures of  $TlCl$  and  $NH_4Cl$  used in this study are taken, in the case of  $TlCl$  ( $a_0 = 3.834 \text{ \AA}$ ) and  $NH_4Cl$  ( $a_0 = 3.8756 \text{ \AA}$ ) from Wyckoff (1965).

In the case of the hexachloroplatinates considered, all the salts possess the anti-fluorite structure with cell constants:

$$K_2PtCl_6 (a_0 = 9.755 \text{ \AA}); Rb_2PtCl_6 (a_0 = 9.901 \text{ \AA}); Cs_2PtCl_6 (a_0 = 10.215 \text{ \AA});$$

$$Tl_2PtCl_6 (a_0 = 9.779 \text{ \AA}) \quad \text{and} \quad (NH_4)_2PtCl_6 (a_0 = 9.858 \text{ \AA})$$

(Wyckoff 1965).

Herzig, Jenkins & Neckel (1976) have expanded  $U_{elec}$ , the electrostatic energy for these salts, as a function of the cell length  $a$  and internal Pt-Cl distance  $d$  and the charge distribution  $q_{Cl}$  on the terminal chlorine atoms of the complex ion, and have determined the values of the coefficients  $A_0$ ,  $A_p$  and  $B_p$  for salts having the  $K_2PtCl_6$  (antifluorite) structure:

$$U_{elec} = \frac{K}{a} \left\{ A_0 + \left( \sum_{\substack{p=2 \\ \text{even}}}^{\infty} A_p \left( \frac{d}{a} \right)^p q_{Cl} + \left( \sum_{\substack{p=2 \\ \text{even}}}^{\infty} B_p \left( \frac{d}{a} \right)^p \right) q_{Cl}^2 \right\}, \quad (33)$$

whereupon

$$\begin{aligned} \left( \frac{\partial U_{elec}}{\partial a} \right)_{a=a_0} &= \left[ \frac{K}{a_0} \left( \frac{\partial M_{elec}}{\partial a} \right)_{a=a_0} - K \frac{M_{elec}}{a_0^2} \right] \\ &= -\frac{K}{a_0^2} \left\{ A_0 + \sum_{\substack{p=2 \\ \text{even}}}^{\infty} (p+1) A_p \left( \frac{d}{a} \right)^p q_{Cl} + \sum_{\substack{p=2 \\ \text{even}}}^{\infty} (p+1) B_p \left( \frac{d}{a} \right)^p q_{Cl}^2 \right\}, \end{aligned} \quad (34)$$

where  $M_{elec}$  is the electrostatic Madelung constant based on  $a_0$ .

In the calculation of  $U_{ad}$  and  $U_{qd}$ , by virtue of the dependence of  $c_{ij}$  and  $d_{ij}$  on  $Q_i$  and  $Q_j$ , which in turn depend on  $\alpha_i$  and  $\alpha_j$ , the polarizabilities we are obliged to select, in the case of the alkali halides, values for  $\alpha$  from the numerous theoretical and experimental determinations of the electronic polarizabilities of the alkali metal and halide ions in the literature. We considered, in the course of this work, five different sets of polarizability data. Two of these sets, that of Pauling (1927) (who used the quadratic Stark effect as the source of data) and that of Tessman, Kahn & Shockley (1953) (who used refractive index measurements) were obvious sources to use for  $\alpha$  because of the range of ions for which polarizabilities are quoted. The latter set have received criticism (Pirenne & Kartheuser 1964; Jaswal & Sharma 1973) on the grounds that invalid minimization procedures were adopted in working up the results. A further two sources of polarizabilities, which also use



## CALCULATIONS

all constants used in this study are taken from sources which are well established. For the sodium chloride  $M_{elec}$  is 3.49513 (Waddington 1959) and for the type II  $M_{elec}$  is 2.035356 (Waddington 1959), the characteristic distance. The computation of

the  $U_{elec}$  used in this study are taken, in the case of sodium chloride, from Wyckoff (1965). For the other salts considered, all the salts possess the anti-

structure  $(a_0 = 9.901 \text{ \AA})$ ;  $\text{Cs}_2\text{PtCl}_6$  ( $a_0 = 10.215 \text{ \AA}$ ); and  $(\text{NH}_4)_2\text{PtCl}_6$  ( $a_0 = 9.858 \text{ \AA}$ )

have expanded  $U_{elec}$ , the electrostatic energy, in terms of length  $a$  and internal Pt-Cl distance  $d$  and the number of terminal chlorine atoms of the complex ion, and the coefficients  $A_0$ ,  $A_p$  and  $B_p$  for salts having the

$$U_{elec} = \left( \frac{d}{a} \right)^p q_{Cl} + \left( \sum_{p=2}^{\infty} B_p \left( \frac{d}{a} \right)^p \right) q_{Cl}^2, \quad (33)$$

$$K \frac{M_{elec}}{a_0^3} \quad (34)$$

$$1) A_p \left( \frac{d}{a} \right)^p q_{Cl} + \sum_{p=2}^{\infty} (p+1) B_p \left( \frac{d}{a} \right)^p q_{Cl}^2, \quad (35)$$

where  $K$  is a constant based on  $a_0$ .

By virtue of the dependence of  $c_{ij}$  and  $d_{ij}$  on  $a$  and  $\alpha$ , the polarizabilities we are obliged to use values for  $\alpha$  from the numerous theoretical calculations of the electronic polarizabilities of the alkali halides. We considered, in the course of this work, (a) Two of these sets, that of Pauling (1927) (which is the source of data) and that of Tessman, (b) refractive index measurements (which were obvious sources of ions for which polarizabilities are quoted. (c) Data from Pirenne & Kartheuser 1964; Jaswal & Kartheuser 1964; and (d) valid minimization procedures were adopted from various sources of polarizabilities, which also use

refractive index measurements, have been considered; namely those of Pirenne & Kartheuser (1964) (who assume a non-additive law) and those of Jaswal & Sharma (1973). A further set of polarizabilities was considered, due to Michael (1969) (average values adopted) who used photo-elastic data for the determinations. Several points regarding these sets are of note: (i) the values of Tessman *et al.* values differ greatly (up to 40 %) from the others, especially for the cations; (ii) Pauling's values differ from the other sets for the anions (up to 25 %); (iii) all the sets, with the exception of those generated by Michael have assumed  $\alpha_{Li^+} = 0.029 \text{ \AA}$  (the quantum-mechanically confirmed free ion value) (Pauling 1927).

The characteristic energy  $\epsilon_1$  of an ion has a much reduced parametric dependence on  $U_{dd}$  and  $U_{qd}$  than has the polarizability  $\alpha$ . The parameter  $\epsilon_+$  for the cation was taken as

$$\epsilon_+ = 0.9 I_2, \quad (36)$$

where  $I_2$  is the second ionization ( $M^+ \rightarrow M^{2+}$ ) potential. The corresponding characteristic energy for the anion  $\epsilon_-$  was found from Mayer's (1933) experimental  $Q_i$  values, in conjunction with individual values of  $\alpha$ .

Two sources of electron number,  $p_i$ , were employed in this study for incorporation into equation (28): the first sets  $p_{Li^+} = 2$ ,  $p_M$  ( $M = \text{Na, K, Rb and Cs}$ ) = 8 and  $p_X$  ( $X = \text{F, Cl, Br and I}$ ) = 8, while the second approach uses the geometric mean of these values with those obtained by application of the Herzfeld & Woolf (1928) equation:

$$p_i = \frac{4\pi^2 m e^2 \alpha_i}{h^2 c^2}, \quad (37)$$

where  $h_p$  is Planck's constant and  $m$  is the mass of the electron.

In the case of the hexachloroplatinate, the derivatives  $(\partial U_{dd}/\partial a)_{a=a_0}$  and  $(\partial U_{qd}/\partial a)_{a=a_0}$  are evaluated using the polarizabilities of Pirenne & Kartheuser (1964), treating the  $\text{PtCl}_6^{4-}$  ion as though it could be regarded as being comprised of six chloride ions (Jenkins 1977). The electron numbers were taken as 8 apart from the case of  $\text{Ti}^{4+}$  when the Herzfeld and Woolf formula above was employed. The summations necessary for the above derivatives took the form of equations (24), (25) and (26).

The equations for  $(\partial U_r/\partial a)_{a=a_0}$  took the form of equation (29) and (31) for the  $\text{MX}$  and  $\text{M}_2\text{PtCl}_6$  salts respectively.

The calculations we have made for  $U_{pot}(\text{MX})$  were carried out for three values of  $\rho$  (0.333, 0.345 and 0.36  $\text{\AA}$ ) to justify, if possible, our contention that variation in  $\rho$  makes very little difference to the final  $U_{pot}(\text{MX})$  values. In the case of the  $\text{M}_2\text{PtCl}_6$  salts  $\rho$  was taken to be 0.345  $\text{\AA}$  throughout.

## 4. RESULTS

We have not attempted to reproduce our results in full in this paper, they are available elsewhere (Jenkins & Pratt 1976b). Instead, we have chosen to quote the set of radii which we regard as optimized 'basic' radii judged on the grounds of

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internal self-consistency (table 1). The effect of choosing any one of five sets of polarizability data rather than any other produces a variation in the radii which in turn produces a variation in  $U_r$  which offsets the associated change in  $U_{ed}$  and  $U_{ad}$  effected by the particular choice made (for numerical details see Jenkins & Pratt 1976b).

TABLE 1. OPTIMIZED SET OF 'BASIC' RADII FOR ALKALI METAL AND HALIDE IONS DERIVED FROM THIS WORK (RADII IN Å)

Ion	$\rho = 0.333 \text{ Å}$		$\rho = 0.345 \text{ Å}$		$\rho = 0.360 \text{ Å}$	
	$p_i(\text{VE})$	$p_i(\text{HW})$	$p_i(\text{VE})$	$p_i(\text{HW})$	$p_i(\text{VE})$	$p_i(\text{HW})$
Li <sup>+</sup>	0.539	0.511	0.424	0.398	0.290	0.268
Na <sup>+</sup> †	0.940	0.940	0.875	0.875	0.810	0.810
K <sup>+</sup>	1.241	1.241	1.191	1.189	1.143	1.141
Rb <sup>+</sup>	1.365	1.368	1.317	1.318	1.273	1.273
Cs <sup>+</sup>	1.518	1.526	1.465	1.472	1.415	1.421
F <sup>-</sup>	1.079	1.129	1.133	1.187	1.181	1.239
Cl <sup>-</sup>	1.472	1.500	1.512	1.543	1.547	1.580
Br <sup>-</sup>	1.598	1.624	1.634	1.662	1.666	1.696
I <sup>-</sup>	1.787	1.811	1.818	1.851	1.844	1.872

$p_i(\text{VE})$ ,  $p_i$  is equal to the number of valence electrons;  $p_i(\text{HW})$ ,  $p_i$  is obtained from the geometric mean of  $p_i(\text{VE})$  and the value of  $p_i$  obtained from Herzfeld & Woolf (1928, eq. (37)).  
† Values fixed for this ion (see text).

The results in table 1, which arise from choosing the polarizabilities derived from Pirenne and Kartheuser's work for the ions involved, are used for the extensions of the method to salts containing complex ions and having cubic lattices.

We recompute, in table 2, the lattice potential energies of the alkali metal halides and compare these with the recommended values suggested by Jenkins & Waddington (1977), which are averages of the results for the lattice potential energy by Cubbiciotti (1959, 1961a, b), Tsai (1962, 1964) and Tosi (1963, 1964).

As mentioned when discussing equation (2), it is necessary for the present method to assign the radius to one ion. The Na<sup>+</sup> ion was chosen and its radius fixed at 0.940 Å (for  $\rho = 0.333 \text{ Å}$ ), at 0.875 Å (for  $\rho = 0.345 \text{ Å}$ ) and at 0.810 Å (for  $\rho = 0.360 \text{ Å}$ ). The iterative procedure described earlier ensured that these values were optimized. The first two values arise in the work of Huggins (1937), the third is derived from the assumption of a rectilinear relationship between  $\bar{r}$  and  $\rho$ . Several points emerge regarding the results: (i) The variation of  $\rho$ , while reflected in quite a considerable variation in the basic radii, does not affect the value of  $U_r$  and therefore of  $U_{\text{pot}}$  markedly. This is the situation we have always claimed when repulsion energies are written as sums of exponential terms. (ii) The agreement between the lattice energies calculated in this study and those selected by Jenkins & Waddington (after considered appraisal of all the calculations reported in the literature from 1959 to date) as being the most reliable is remarkable. (iii) The agreement between the 'basic' radii of Huggins and those derived (but not reproduced here) using

of choosing any one of five sets of radii produces a variation in the radii which is the associated change in  $U_{ad}$  and  $U_{at}$ . Numerical details see Jenkins & Pratt

# RADII FOR ALKALI METAL THIS WORK (RADII IN Å)

$\rho = 0.360 \text{ Å}$		
$p_i(\text{HW})$	$p_i(\text{VE})$	$p_i(\text{HW})$
0.398	0.290	0.268
0.875	0.810	0.810
1.189	1.143	1.141
1.318	1.273	1.273
1.472	1.415	1.421
1.187	1.181	1.239
1.543	1.547	1.580
1.662	1.666	1.696
1.851	1.844	1.872

electrons:  $p_i(\text{HW})$ ,  $p_i$  is obtained from the values from Herzfeld & Woolf (1928, eq. (37)).

Using the polarizabilities derived from the values involved, are used for the extensions of the radii and having cubic lattices.

Latent energies of the alkali metal halides and values suggested by Jenkins & Waddington (1962, 1964) and Tosi (1963, 1964).

It is necessary for the present method that the radius was chosen and its radius fixed at 0.345 Å and at 0.810 Å (for  $\rho = 0.36 \text{ Å}$ ).

It is assumed that these values were optimized. (iii) The agreement between the lattice energies (1937), the third is derived from the values between  $\bar{r}$  and  $\rho$ . Several points emerge while reflected in quite a considerable

the value of  $U_i$  and therefore of  $U_{pot}$  is claimed when repulsion energies are

The agreement between the lattice energies selected by Jenkins & Waddington

conditions reported in the literature from

marked. (iii) The agreement between

values (but not reproduced here) using

## 'Basic' radii and repulsion energies in ionic crystals

TABLE 2. COMPUTED LATTICE ENERGIES ( $\text{KJ MOL}^{-1}$ ) FROM THE PRESENT STUDY AS COMPARED WITH THE RECOMMENDED VALUES SUGGESTED BY JENKINS & WADDINGTON (J & W) (1977)

MX	$U_{ad}$		$U_{at}$		$U_{pot}$		J & W $U_{ad}(\text{MX})$
	$p(\text{VE})$	$p(\text{HW})$	$\rho = 0.333 \text{ Å}$	$\rho = 0.345 \text{ Å}$	$\rho = 0.360 \text{ Å}$	$\rho = 0.345 \text{ Å}$	
LiF	1.1	2.2	193.2	191.5	188.7	1032.6	1030.9
LiCl	2.2	3.5	128.8	129.7	129.8	844.6	844.6
LiBr	2.4	3.7	111.8	112.9	113.9	800.3	799.0
LiI	2.6	4.6	101.1	104.6	104.3	741.6	738.0
NaF	2.2	3.4	185.3	174.2	179.3	911.7	905.8
NaCl	2.5	3.7	119.0	121.4	124.4	773.8	770.4
NaBr	2.5	3.7	106.1	108.8	111.7	737.9	735.2
NaI	2.6	4.1	91.0	94.6	95.7	691.0	687.3
KF	3.1	4.1	136.0	143.9	151.2	807.1	799.2
KCl	3.2	4.3	101.8	108.0	109.9	705.8	701.6
KBr	3.1	4.2	93.8	97.0	100.3	677.4	674.2
KI	3.0	4.4	82.7	86.1	87.4	639.3	635.9
RbF	3.7	4.5	127.8	135.6	143.3	771.7	763.9
RbCl	3.6	4.5	94.8	99.1	103.2	681.7	677.3
RbBr	3.6	4.5	91.7	94.9	98.4	655.9	652.7
RbI	3.4	4.3	77.8	81.0	82.4	620.6	617.4
CaF	5.7	5.8	117.9	122.9	127.5	738.7	733.8
CaCl	6.1	6.5	95.5	99.4	103.2	647.3	643.4
CaBr	5.9	6.5	89.7	93.4	97.4	626.8	623.2
CaI	5.4	6.5	76.4	81.0	83.6	596.4	591.8

†  $U_{ad}$  given for two choices of  $p_i$  (see text).

‡  $U_i$  quoted is average of two  $U_i$  values calculated from equation (27) using the two sets of radii ( $p(\text{VE})$  and  $p(\text{HW})$ ) in table 1.

similar data leads us to have confidence in the use of the radii given in table 1 which are based on what we regard as more reliable data.

Choosing  $\bar{r}_{\text{Cl}^-}$  as being equal to 1.512 Å (table 1) corresponding to  $\rho = 0.345$  Å we considered the salts TlCl and  $\text{NH}_4\text{Cl}$  and obtained, by solution of equation (6):

$$\bar{r}_{\text{Tl}^+} = 1.370 \text{ Å}, \quad (38)$$

$$\bar{r}_{\text{NH}_4^+} = 1.265 \text{ Å}. \quad (39)$$

TABLE 3. RESULTS FOR TlCl AND  $\text{NH}_4\text{Cl}$ 

	TlCl	$\text{NH}_4\text{Cl}$	notes
$U_{\text{elec}}$	737.5	729.6	$\text{kJ mol}^{-1}$
$a_0$ (Å)	3.834	3.8756	shortest distance
$\epsilon_{\text{M}^+}$	29.4	41.4	$10^{12} \text{ erg molecule}^{-1}$
$\epsilon_{\text{Cl}^-}$	17.2	17.2	$10^{12} \text{ erg molecule}^{-1}$
$\alpha_{\text{M}^+}$	3.880	1.656	Å <sup>3</sup>
$\alpha_{\text{Cl}^-}$	2.995	2.995	Å <sup>3</sup> Pirene & Kartheuser (1964)
$U_{\text{el}}$	109.8	48.1	$\text{kJ mol}^{-1}$
$U_{\text{el}}^0$	14.0	5.2	$\text{kJ mol}^{-1}$
$U_i$	153.0	106.2	$\text{kJ mol}^{-1}$
$U_{\text{pot}}(\text{MCl})$	708.3	676.7	$\text{kJ mol}^{-1}$ (this work.)

The results for individual terms are given in table 3 for  $\rho = 0.345$  Å. Using  $\bar{r}_{\text{K}^+}$ ,  $\bar{r}_{\text{Rb}^+}$  and  $\bar{r}_{\text{Cs}^+}$  from table 1 and  $\bar{r}_{\text{Tl}^+}$  and  $\bar{r}_{\text{NH}_4^+}$  from equations (38) and (39), we calculate  $\bar{r}_{\text{PtCl}_2^-}$  in the cases of the salts  $\text{M}_2\text{PtCl}_6$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$  and  $\text{NH}_4$ ) having the antifluorite structure. Taking  $\rho = 0.345$  Å, the solution of equation (3) gives the curves reproduced in figure 1, which take the parametric form

$$\bar{r}_{\text{PtCl}_2^-} = \rho \ln [\phi_0 + (\phi_1 + \phi_2 q_{\text{Cl}} + \phi_3 q_{\text{Cl}}^2)^{\frac{1}{2}}], \quad (40)$$

where  $\phi_0$ ,  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  are  $\rho$  dependent 'constants' arising from the solution of equation (3), since

$$\exp\left(\frac{\bar{r}_{\text{PtCl}_2^-}}{\rho}\right) = \frac{[-\theta'_2 \pm (\theta'_2{}^2 - 4\theta'_3\theta'_1)^{\frac{1}{2}}]}{2\theta'_3}, \quad (41)$$

whereupon 
$$\bar{r}_{\text{PtCl}_2^-} = \rho \ln \left[ -\frac{\theta'_2}{2\theta'_3} \pm \left( \frac{\theta'_2{}^2}{4\theta'_3{}^2} - \frac{\theta'_1}{\theta'_3} \right)^{\frac{1}{2}} \right] \quad (42)$$

and since  $\theta'_1$  is a quadratic function of the charge  $q_{\text{Cl}}$  on the terminal atom of the ion, by virtue of the equation

$$U_{\text{elec}} = \sum_{i=0}^2 D_i q_{\text{Cl}}^i \quad (43)$$

and the equation

$$K \left( \frac{\partial M_{\text{elec}}}{\partial a} \right)_{a=a_0} = \sum_{i=1}^2 E_i q_{\text{Cl}}^i; \quad (44)$$

hence

$$\theta'_1 = \sum_{i=0}^2 F_i q_{\text{Cl}}^i \quad (45)$$

use of the radii given in table 1 which  
data.

ble 1) corresponding to  $\rho = 0.345 \text{ \AA}$  we  
ained, by solution of equation (6):

$$70 \text{ \AA}, \quad (38)$$

$$65 \text{ \AA}. \quad (39)$$

TlCl and NH<sub>4</sub>Cl

notes

kJ mol<sup>-1</sup>

shortest distance

10<sup>18</sup> erg molecule<sup>-1</sup>10<sup>18</sup> erg molecule<sup>-1</sup>Å<sup>3</sup>) Pirenne & Kartheuser (1964)kJ mol<sup>-1</sup>kJ mol<sup>-1</sup>kJ mol<sup>-1</sup>kJ mol<sup>-1</sup> (this work.)

in table 3 for  $\rho = 0.345 \text{ \AA}$ . Using  $\bar{r}_{\text{K}^+}$ ,  
from equations (38) and (39), we  
Cl<sub>6</sub> (M = K, Rb, Cs, Tl and NH<sub>4</sub>) having  
the solution of equation (3) gives the  
parametric form

$$\phi_2 q_{\text{Cl}} + \phi_3 q_{\text{Cl}}^2, \quad (40)$$

constants' arising from the solution of

$$\pm \frac{(\theta_2'^2 - 4\theta_3'\theta_1')^{1/2}}{2\theta_3'}, \quad (41)$$

$$\pm \left( \frac{\theta_2'^2 - \theta_1'}{4\theta_3' - \theta_1'} \right)^{1/2} \quad (42)$$

charge  $q_{\text{Cl}}$  on the terminal atom of the

$$D_i q_{\text{Cl}}^i \quad (43)$$

$$\sum_{i=1}^2 E_i q_{\text{Cl}}^i; \quad (44)$$

$$q_{\text{Cl}} \quad (45)$$

so that in equation (40)

$$\phi_0 = -\theta_2'/2\theta_3', \quad \phi_1 = \theta_2'/4\theta_3' - F_0/\theta_3' \quad (46, 47)$$

$$\phi_2 = -F_1/\theta_3', \quad \phi_3 = -F_2/\theta_3'. \quad (48, 49)$$

Values of  $\phi_0$ ,  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  for the salts M<sub>2</sub>PtCl<sub>6</sub> are listed in table 4. Figure 1 gives  
a plot of  $\bar{r}_{\text{PtCl}_6^-}$  against  $q_{\text{Cl}}$  for these salts.

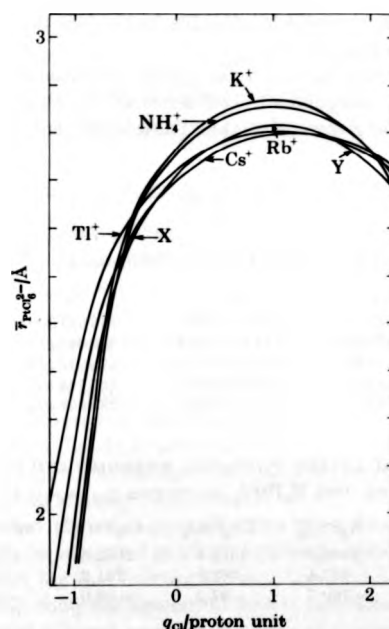


FIGURE 1. Plot of 'basic' radius of hexachloroplatinate ion,  $\bar{r}_{\text{PtCl}_6^-}$  against the charge on the terminal chlorine atoms  $q_{\text{Cl}}$  of the  $\text{PtCl}_6^-$  ion for K<sub>2</sub>PtCl<sub>6</sub>, Rb<sub>2</sub>PtCl<sub>6</sub>, Cs<sub>2</sub>PtCl<sub>6</sub>, Tl<sub>2</sub>PtCl<sub>6</sub> and (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> salts.

In figure 1 the curves are similar in form on account of the isostructural nature of the salts considered and thus the intersections at regions X and Y have no precise quantitative interpretation. Clearly we require a salt of the type M<sub>2</sub>PtCl<sub>6</sub> of different (not antiferroite) structure to quantify the intersections completely. Clearly the intersection points X (figure 1) are allied to the chemical charge distribution situation as it exists in  $\text{PtCl}_6^{2-}$  and the intersections lie close to the value of  $q_{\text{Cl}}$  predicted for the ion from n.q.r. work (Kubo & Nakamura 1966) which corresponds to  $q_{\text{Cl}} = -0.44$  and to the value assigned from molecular orbital calculations by

(S)

Cotton & Harris (1967) which corresponds to  $q_{Cl} = -0.445$ . If we assign  $q_{Cl}$  to be  $-0.44$  this generates, for  $\rho = 0.345 \text{ \AA}$ , the values  $\bar{r}_{PtCl_4^-}$  equal to  $2.60 \text{ \AA}$  (for potassium salt),  $2.56 \text{ \AA}$  (for rubidium salt),  $2.58 \text{ \AA}$  (for caesium salt),  $2.62 \text{ \AA}$  (for thallium salt) and  $2.60 \text{ \AA}$  (for the ammonium salt), averaging to

$$\bar{r}_{PtCl_4^-} = 2.59 \text{ \AA}. \quad (50)$$

In the calculations of  $U_r$  for these salts the *actual* (rather than the average) radii generated were used. The rationale for this lies in the fact that the Pt-Cl distance varies by 3 % in these compounds.

Table 5 gives the results for the total lattice potential energies of the salts considered. The charge independent coefficients of the electrostatic energy and related derivative are also given in the table. These coefficients have been defined in

TABLE 4. VALUES OF  $\phi_0$ ,  $\phi_1$ ,  $\phi_2$  AND  $\phi_3$  IN RELATION:

$$\bar{r}_{PtCl_4^-} = \rho \ln [\phi_0 + (\phi_1 + \phi_2 q_{Cl} + \phi_3 q_{Cl}^2)]$$

FOR  $\rho = 0.345 \text{ \AA}$  FOR  $M_2PtCl_6$  SALTS

salt	$\phi_0$	$\phi_1$	$\phi_2$	$\phi_3$
K <sub>2</sub> PtCl <sub>6</sub>	-52361.0	3067748210	235654900	-117939627
Rb <sub>2</sub> PtCl <sub>6</sub>	-84722.6	7619623830	289049554	-131283992
Cs <sub>2</sub> PtCl <sub>6</sub>	-166976.0	28721523400	483016132	-198805278
Tl <sub>2</sub> PtCl <sub>6</sub>	-86170.8	7892303070	230748492	-104804169
(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub>	-70421.0	5382159880	284998492	-142635040

TABLE 5. TOTAL LATTICE POTENTIAL ENERGIES AND COMPONENT TERMS FOR  $M_2PtCl_6$  SALTS FOR  $q_{Cl} = -0.44$

$U_{\text{obs}}$ (kJ mol <sup>-1</sup> )	K <sub>2</sub> PtCl <sub>6</sub>	Rb <sub>2</sub> PtCl <sub>6</sub>	Cs <sub>2</sub> PtCl <sub>6</sub>	Tl <sub>2</sub> PtCl <sub>6</sub>	(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub>
$D_0$	1657.3	1632.8	1582.6	1653.2	1640.0
$D_1$	401.4	368.0	331.2	372.6	397.2
$D_2$	-100.7	-84.2	-69.0	-85.3	-99.7
$K \left( \frac{\partial M_{\text{obs}}}{\partial a} \right)_{a=a_0}$ (kJ mol <sup>-1</sup> )					
$E_1$	-1365.3	-1262.6	-1145.8	-1278.3	-1351.1
$E_2$	783.5	656.4	538.9	664.6	775.3
$\alpha^+$ (Å <sup>2</sup> )	1.029	1.570	2.641	3.880	1.656
$\epsilon_+$ (erg molecule <sup>-1</sup> × 10 <sup>-12</sup> )	45.84	39.63	36.17	29.42	41.09
$U_{\text{int}}$ (kJ mol <sup>-1</sup> )	118.8	129.1	145.8	246.6	142.3
$U_{\text{ext}}$ (kJ mol <sup>-1</sup> )	9.8	11.4	15.5	27.3	13.4
$q_{Cl} = -0.44$					
$U_{\text{obs}}$ (kJ mol <sup>-1</sup> )	1461.2	1454.6	1423.9	1472.7	1445.9
$U_r$ (kJ mol <sup>-1</sup> )	121.7	131.2	141.1	201.0	133.6
$\bar{r}_{PtCl_4^-}$ (Å)	2.60	2.56	2.58	2.62	2.60
$\bar{r}_{M^+}$ (Å)	1.19	1.32	1.46	1.37	1.26
$U_{\text{pot}}$ (kJ mol <sup>-1</sup> )	1468.2	1463.9	1443.8	1545.7	1468.0

ends to  $q_{Cl} = -0.445$ . If we assign  $q_{Cl}$  to be  $\text{\AA}$ , the values  $\bar{r}_{PtCl_6}$  equal to  $2.60 \text{ \AA}$  (for salt),  $2.58 \text{ \AA}$  (for caesium salt),  $2.62 \text{ \AA}$  (for ammonium salt), averaging to

$$\bar{r}_{PtCl_6} = 2.59 \text{ \AA}. \quad (50)$$

the actual (rather than the average) radii this lies in the fact that the Pt-Cl distance

total lattice potential energies of the salts coefficients of the electrostatic energy and able. These coefficients have been defined in

$\phi_1, \phi_2$  AND  $\phi_3$  IN RELATION:

$$+ (\phi_1 + \phi_2 q_{Cl} + \phi_3 q_{Cl}^2)^{1/2}$$

FOR  $M_2PtCl_6$  SALTS

$\phi_1$	$\phi_2$	$\phi_3$
748210	235 654 900	-117 939 627
623 830	289 049 554	-131 283 992
523 400	483 016 132	-198 805 278
303 070	230 748 492	-104 804 169
159 880	284 998 492	-142 635 040

ENTIAL ENERGIES AND COMPONENT

SALTS FOR  $q_{Cl} = -0.44$

$b_1PtCl_6$	$Ca_2PtCl_6$	$Tl_2PtCl_6$	$(NH_4)_2PtCl_6$
632.8	1582.6	1653.2	1640.0
368.0	331.2	372.6	397.2
-84.2	-69.0	-85.3	-99.7
262.6	-1145.8	-1278.3	-1351.1
656.4	538.9	664.6	775.3
1.570	2.641	3.880	1.656
39.63	36.17	29.42	41.09
129.1	145.8	246.6	142.3
11.4	15.5	27.3	13.4
454.6	1423.9	1472.7	1445.9
131.2	141.1	201.0	133.6
2.56	2.58	2.62	2.60
1.32	1.46	1.37	1.28
463.9	1443.8	1545.7	1468.0

# 'Basic' radii and repulsion energies in ionic crystals 129

equations (43) and (44). The values for  $U_r$  and  $U_{pot}(M_2PtCl_6)$  are quoted for  $q_{Cl} = -0.44$  for the salts considered and we assign

$$U_{pot}(K_2PtCl_6) = 1468 \text{ kJ mol}^{-1}, \quad (51)$$

$$U_{pot}(Rb_2PtCl_6) = 1464 \text{ kJ mol}^{-1}, \quad (52)$$

$$U_{pot}(Cs_2PtCl_6) = 1444 \text{ kJ mol}^{-1}, \quad (53)$$

$$U_{pot}(Tl_2PtCl_6) = 1546 \text{ kJ mol}^{-1}, \quad (54)$$

$$U_{pot}((NH_4)_2PtCl_6) = 1468 \text{ kJ mol}^{-1}. \quad (55)$$

The corresponding lattice potential energies of  $TlCl$  and  $NH_4Cl$  were

$$U_{pot}(TlCl) = 708 \text{ kJ mol}^{-1}, \quad (56)$$

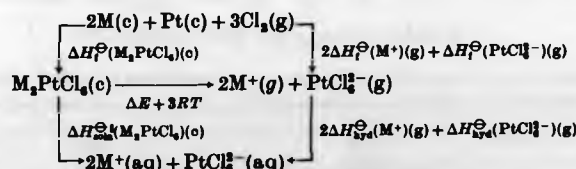
$$U_{pot}(NH_4Cl) = 677 \text{ kJ mol}^{-1}. \quad (57)$$

## 4. DISCUSSION

Indicative of the success of the method proposed here must be the consistency obtained for the 'basic' radius of the hexachloroplatinate ion (shown by the approximate constancy of  $\bar{r}_{PtCl_6}$  in table 5 irrespective of the cation). We consider now the repulsion energy,  $U_r$ , the lattice potential energy,  $U_{pot}$  and the ancillary thermochemical data which can be generated from these calculations. The potassium salt,  $K_2PtCl_6$ , has received considerable attention in the literature over the last five years (Hartley 1972; Lister, Nyburg & Poyntz 1974; De Jonge 1976; Jenkins 1977). Jenkins (1977) has referred to the discrepancy in the values obtained from the empirical and the Born-Landé approaches. Table 6 gives the collected results from the literature. The column headings in this table indicate the equations employed to calculate the lattice and repulsion energies in each case.

It will be seen that the contention (Jenkins 1977) that the repulsion energy in  $K_2PtCl_6$  is of the order of  $120 \text{ kJ mol}^{-1}$  is completely upheld by the present study. Moreover the result for this salt for  $U_r$  from the Jenkins & Waddington (1975) equation is in almost complete agreement with  $U_r$  calculated from the present work. The former equation is based on a consideration of nearest neighbour interactions only and takes the repulsion energy in the form of equation (32). The fact that  $U_r$  in the two studies differ by only  $3 \text{ kJ mol}^{-1}$  indicates that the  $PtCl_6^{2-}$ - $PtCl_6^{2-}$  ion interactions do not substantially contribute to  $U_r$  in  $K_2PtCl_6$ .

If we consider the Born-Fajans-Haber cycle (Morris & Short 1969) for  $M_2PtCl_6$ , we have:



(S)



TABLE 6. LITERATURE CALCULATIONS OF  $U_{\text{elec}}$ ,  $U_{\text{dd}}$ ,  $U_r$  AND  $U_{\text{pot}}$  FOR  $\text{K}_2\text{PtCl}_6$ 

kJ mol <sup>-1</sup>	Hartley (1972)		
	Born-Mayer equation	Kapustinskii equation	
	$U_{\text{pot}} = U_{\text{elec}} \left(1 - \frac{\rho}{r_{\text{an}}}\right)$	$U_{\text{pot}} = \frac{1202\nu z_+ z_-}{r_{\text{an}}} \left(1 - \frac{\rho}{r_{\text{an}}}\right)$	
	$U_r = \frac{\rho}{r_{\text{an}}} U_{\text{elec}}$ $\rho = 0.345 \text{ \AA}$	$U_r = \frac{1202\nu z_+ z_- \rho}{r_{\text{an}}^2}$ $\rho = 0.345 \text{ \AA}$	
$U_{\text{elec}}$	1680	1744	
$U_r$	140	146	
$U_{\text{dd}}$	—	—	
$U_{\text{pot}}(\text{K}_2\text{PtCl}_6)$	1540	1598	

kJ mol <sup>-1</sup>	Lister, Nyburg & Poyntz (1974)		
	extended Born-Landé equation	simple Born-Landé equation	Kapustinskii equation
	$U_{\text{pot}} = U_{\text{elec}} \left(1 - \frac{1}{n}\right) + U_{\text{dd}} \left(1 - \frac{6}{n}\right)$	$U_{\text{pot}} = U_{\text{elec}} \left(1 - \frac{1}{n}\right)$	$U_{\text{pot}} = \frac{1214\nu z_+ z_-}{r_{\text{an}}} \times \left(1 - \frac{\rho}{r_{\text{an}}}\right)$
	$U_r = \frac{1}{n} [U_{\text{elec}} + 6U_{\text{dd}}]$ $n = 9, q_{\text{Cl}} = -0.44$	$U_r = \frac{1}{n} U_{\text{elec}}$ $n = 8$	$U_r = \frac{1214\nu z_+ z_- \rho}{r_{\text{an}}^2}$ $\rho = 0.345 \text{ \AA}$
$U_{\text{elec}}$	1385	1657	1713
$U_r$	238	207	141
$U_{\text{dd}}$	126	—	—
$U_{\text{pot}}(\text{K}_2\text{PtCl}_6)$	1273	1450	1572

kJ mol <sup>-1</sup>	De Jonge (1976) extended Born-Landé equation	Jenkins (1977) Jenkins & Waddington equation (see reference)
	$U_{\text{pot}} = U_{\text{elec}} \left(1 - \frac{1}{n}\right) + U_{\text{dd}} \left(1 - \frac{6}{n}\right)$	$U_r = \frac{\rho}{\alpha_0} \left[ U_{\text{elec}} + 6U_{\text{dd}} + 8U_{\text{dd}} - K \left( \frac{\partial M_{\text{elec}}}{\partial \alpha} \right)_{\alpha=\alpha_0} \right]$
	$U_r = \frac{1}{n} [U_{\text{elec}} + 6U_{\text{dd}}]$ $n = 8.5, q_{\text{Cl}} = -0.44$	$\rho = 0.345 \text{ \AA}, q_{\text{Cl}} = -0.44$
$U_{\text{elec}}$	1459	1461
$U_r$	256	125
$U_{\text{dd}}$	120	132
$U_{\text{pot}}(\text{K}_2\text{PtCl}_6)$	1323	1468



ley (1972)

Kapustinskii  
equation

$$U_{\text{pot}} = \frac{1202vz_+z_-}{r_{\text{an}}} \left(1 - \frac{\rho}{r_{\text{an}}}\right)$$

$$U_r = \frac{1202vz_+z_- \rho}{r_{\text{an}}^2}$$

$$\rho = 0.345 \text{ \AA}$$

1744

146

1598

ster, Nyburg &amp; Poyntz (1974)

simple Born-  
Landé equationKapustinskii  
equation

$$U_{\text{pot}} = \frac{1214vz_+z_-}{r_{\text{an}}}$$

$$U_{\text{pot}} = U_{\text{elec}} \left(1 - \frac{1}{n}\right)$$

$$\times \left(1 - \frac{\rho}{r_{\text{an}}}\right)$$

$$U_r = \frac{1}{n} U_{\text{elec}}$$

$$U_r = \frac{1214vz_+z_- \rho}{r_{\text{an}}^2}$$

$$\rho = 0.345 \text{ \AA}$$

1657

207

1450

1713

141

1572

Jenkins (1977)

Jenkins &  
Waddington equation  
(see reference)

$$\left(1 - \frac{\rho}{n}\right) U_r = \frac{\rho}{\alpha_0} \left[ U_{\text{elec}} + 6U_{\text{dd}} + 8U_{\text{dd}} - K \left( \frac{\partial M_{\text{dd}}}{\partial \alpha} \right)_{\alpha=\alpha_0} \right]$$

$$-0.44 \quad \rho = 0.345 \text{ \AA}, \quad q_{\text{Cl}} = -0.44$$

1461

125

132

1468

## 'Basic' radii and repulsion energies in ionic crystals

131

where  $\Delta E$  is the total internal energy change for the 'lattice energy' step in the cycle and is given by

$$\Delta E = 2E_{M^+} + E_{PtCl_6^-} - E_{M_2PtCl_6}, \quad (58)$$

where  $E_i$  represents the total internal energy of the species  $i$ . If  $M^+$  is a monatomic ion (e.g.  $K^+$ ,  $Rb^+$ ,  $Cs^+$  or  $Tl^+$ ),

$$2E_{M^+} = 3RT. \quad (59)$$

When  $M^+$  is a polyatomic ion (e.g.  $NH_4^+$ )

$$2E_{M^+} = 6RT. \quad (60)$$

Similarly

$$E_{PtCl_6^-} = 3RT, \quad (61)$$

while

$$E_{M_2PtCl_6} = U_{\text{acous}} - U_{\text{pot}}(M_2PtCl_6), \quad (62)$$

where  $U_{\text{acous}}$  is the acoustic energy of the lattice (taken as  $3RT$  per ion), whereupon for salts  $K_2PtCl_6$ ,  $Rb_2PtCl_6$ ,  $Cs_2PtCl_6$  and  $Tl_2PtCl_6$

$$\Delta E + 3RT = U_{\text{pot}}(M_2PtCl_6), \quad (63)$$

while for  $(NH_4)_2PtCl_6$ 

$$\Delta E + 3RT = U_{\text{pot}}((NH_4)_2PtCl_6) + 3RT. \quad (64)$$

Hence for the potassium, rubidium, caesium and thallium salts we have, from the cycle

$$\Delta H_{\text{hyd}}^\circ(PtCl_6^{2-})(g) = \Delta H_{\text{soln}}^\circ(M_2PtCl_6)(c) - U_{\text{pot}}(M_2PtCl_6) - 2\Delta H_{\text{hyd}}^\circ(M^+)(g), \quad (65)$$

$$\Delta H_f^\circ(PtCl_6^{2-})(g) = \Delta H_f^\circ(M_2PtCl_6)(c) + U_{\text{pot}}(M_2PtCl_6) - 2\Delta H_f^\circ(M^+)(g), \quad (66)$$

while for the ammonium salt

$$\Delta H_{\text{hyd}}^\circ(PtCl_6^{2-})(g)$$

$$= \Delta H_{\text{soln}}^\circ[(NH_4)_2PtCl_6](c) - U_{\text{pot}}[(NH_4)_2PtCl_6] - 3RT - 2\Delta H_{\text{hyd}}^\circ(NH_4^+)(g), \quad (67)$$

$$\Delta H_f^\circ(PtCl_6^{2-})(g)$$

$$= \Delta H_f^\circ[(NH_4)_2PtCl_6](c) + U_{\text{pot}}[(NH_4)_2PtCl_6] + 3RT - 2\Delta H_f^\circ(NH_4^+)(g). \quad (68)$$

Coulter, Pitzer & Latimer (1940) have reported  $\Delta H_{\text{soln}}^\circ(K_2PtCl_6)(c) = 56.5 \text{ kJ mol}^{-1}$ . If we use equation (65), applied to  $K_2PtCl_6$ , taking the value for  $U_{\text{pot}}(K_2PtCl_6)$  as given by equation (51) with  $\Delta H_{\text{hyd}}^\circ(K^+)(g) = -330.4 \text{ kJ mol}^{-1}$  (Jenkins & Morris 1976b), we obtain, for  $q_{\text{Cl}} = -0.44$

$$\Delta H_{\text{hyd}}^\circ(PtCl_6^{2-})(g) = -751 \text{ kJ mol}^{-1}. \quad (69)$$

Shidlovskii & Valkina (1961) have reported  $\Delta H_{\text{soln}}^\circ[(NH_4)_2PtCl_6](c) = 49.8 \text{ kJ mol}^{-1}$ . If we use equation (67), taking  $U_{\text{pot}}[(NH_4)_2PtCl_6]$  as given by equation (55), together with  $\Delta H_{\text{hyd}}^\circ(NH_4^+)(g) = -331.4 \text{ kJ mol}^{-1}$  (Jenkins & Morris 1976a), we obtain, for  $q_{\text{Cl}} = -0.44$

$$\Delta H_{\text{hyd}}^\circ(PtCl_6^{2-})(g) = -763 \text{ kJ mol}^{-1}, \quad (70)$$

5-2

(S)

where the latter equation, by virtue of the nature of the treatment of the  $\text{NH}_4^+$  ion as a point charge ion, is possibly less reliable than equation (69). However, simple averaging leads us to assign

$$\Delta H_{\text{hyd}}^\circ(\text{PtCl}_6^{3-})(g) = -757 \text{ kJ mol}^{-1}. \quad (71)$$

Rather than use the literature value of  $\Delta H_f^\circ(\text{K}_2\text{PtCl}_6)(c) (= -1259 \text{ kJ mol}^{-1})$  which is derived from the  $\Delta H_{\text{soln}}^\circ(\text{K}_2\text{PtCl}_6)(c)$  value using  $\Delta H_f^\circ(\text{PtCl}_6^{3-})(\text{aq})$  (Rossini, Wagman, Levine & Jaffe 1952), we calculate  $\Delta H_f^\circ(\text{PtCl}_6^{3-})(g)$  using the equation

$$\Delta H_f^\circ(\text{PtCl}_6^{3-})(g) = \Delta H_f^\circ(\text{PtCl}_6^{3-})(\text{aq}) - 2\Delta H_f^\circ(\text{H}^+)(g) - 2\Delta H_{\text{hyd}}^\circ(\text{H}^+)(g) - \Delta H_{\text{hyd}}^\circ(\text{PtCl}_6^{3-})(g) \quad (72)$$

with the ancillary data  $\Delta H_{\text{hyd}}^\circ(\text{H}^+)(g) = -1100.6 \text{ kJ mol}^{-1}$  (from Jenkins & Morris (1976b)),  $\Delta H_f^\circ(\text{PtCl}_6^{3-})(\text{aq}) = -678 \text{ kJ mol}^{-1}$  (from Goldberg & Hepler 1968), or  $= -674 \text{ kJ mol}^{-1}$  (from Wagman *et al.* 1968) and  $\Delta H_f^\circ(\text{H}^+)(g) = 1536 \text{ kJ mol}^{-1}$  (from Wagman *et al.* 1968), whereupon:  $\Delta H_f^\circ(\text{PtCl}_6^{3-})(g) = -792 \text{ kJ mol}^{-1}$  or  $-788 \text{ kJ mol}^{-1}$ , averaging to

$$\Delta H_f^\circ(\text{PtCl}_6^{3-})(g) = -790 \text{ kJ mol}^{-1}. \quad (73)$$

Using the thermochemical cycle above with  $\text{M}_2\text{PtCl}_6$  replaced by  $\text{BaPtCl}_6$ , we can use the known enthalpy of formation of crystalline barium hexachloroplatinate ( $= -1180 \text{ kJ mol}^{-1}$ ) (Goldberg & Hepler 1968) and  $\Delta H_f^\circ(\text{Ba}^{2+})(g) = 1660 \text{ kJ mol}^{-1}$  (Wagman *et al.* 1968) to find the lattice energy of the salt  $\text{BaPtCl}_6$ . We find

$$U_{\text{pot}}(\text{BaPtCl}_6) = \Delta H_f^\circ(\text{Ba}^{2+})(g) + \Delta H_f^\circ(\text{PtCl}_6^{3-})(g) - \Delta H_f^\circ(\text{BaPtCl}_6)(c) - \frac{1}{2}RT, \quad (74)$$

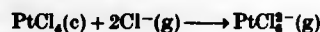
$$U_{\text{pot}}(\text{BaPtCl}_6) = 2047 \text{ kJ mol}^{-1}. \quad (75)$$

In a similar manner since  $\Delta H_f^\circ(\text{Ag}_2\text{PtCl}_6)(c) = -527 \text{ kJ mol}^{-1}$  (Goldberg & Hepler 1968), and  $\Delta H_f^\circ(\text{Ag}^+)(g) = 1019 \text{ kJ mol}^{-1}$  (Wagman *et al.* 1968) we have

$$U_{\text{pot}}(\text{Ag}_2\text{PtCl}_6) = 2\Delta H_f^\circ(\text{Ag}^+)(g) + \Delta H_f^\circ(\text{PtCl}_6^{3-})(g) - \Delta H_f^\circ(\text{Ag}_2\text{PtCl}_6)(c), \quad (76)$$

$$\text{from which } U_{\text{pot}}(\text{Ag}_2\text{PtCl}_6) = 1773 \text{ kJ mol}^{-1}. \quad (77)$$

The chloride ion affinity,  $\overline{\Delta H_{\text{Cl}}}$  of crystalline  $\text{PtCl}_4$  is measured by the process



and is given by the equation

$$\overline{\Delta H_{\text{Cl}}} = \Delta H_f^\circ(\text{PtCl}_6^{3-})(g) - 2\Delta H_f^\circ(\text{Cl}^-)(g) - \Delta H_f^\circ(\text{PtCl}_4)(c) \quad (78)$$

and taking  $\Delta H_f^\circ(\text{Cl}^-)(g) = -233.8 \text{ kJ mol}^{-1}$  (Jenkins & Morris 1976a) and  $\Delta H_f^\circ(\text{PtCl}_4)(c) = -236.4 \text{ kJ mol}^{-1}$  (Wagman *et al.* 1968), we find

$$\overline{\Delta H_{\text{Cl}}} = -116 \text{ kJ mol}^{-1}. \quad (79)$$

Regarding the value for  $\Delta H_{\text{hyd}}^\circ(\text{PtCl}_6^{3-})(g) = -757 \text{ kJ mol}^{-1}$  derived from our calculated lattice energies, this lies midway between the value  $-871 \text{ kJ mol}^{-1}$  (Lister *et al.* 1974) and  $-602 \text{ kJ mol}^{-1}$  (De Jonge 1976), the two values quoted for this quantity in the literature.

nature of the treatment of the  $\text{NH}_4^+$  ion is different from equation (69). However, simple

$$\Delta H_f^\circ(\text{PtCl}_6^{2-}) = -757 \text{ kJ mol}^{-1} \quad (71)$$

if  $\Delta H_f^\circ(\text{K}_2\text{PtCl}_6)(c) = -1259 \text{ kJ mol}^{-1}$  is used as a value using  $\Delta H_f^\circ(\text{PtCl}_6^{2-})(\text{aq})$  (Rossini, 1968) and  $\Delta H_f^\circ(\text{PtCl}_6^{2-})(g)$  using the equation

$$\Delta H_{\text{hyd}}^\circ(\text{H}^+)(g) - \Delta H_{\text{hyd}}^\circ(\text{PtCl}_6^{2-})(g) \quad (72)$$

$1100.6 \text{ kJ mol}^{-1}$  (from Jenkins & Morris, 1968), or  $1100.6 \text{ kJ mol}^{-1}$  (from Goldberg & Hepler 1968), or  $1100.6 \text{ kJ mol}^{-1}$  (from Goldberg & Hepler 1968) and  $\Delta H_f^\circ(\text{H}^+)(g) = 1536 \text{ kJ mol}^{-1}$  (from Rossini, 1968) :  $\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) = -792 \text{ kJ mol}^{-1}$  or

$$\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) = -790 \text{ kJ mol}^{-1} \quad (73)$$

if  $\text{M}_2\text{PtCl}_6$  replaced by  $\text{BaPtCl}_6$ , we can use the crystalline barium hexachloroplatinate (1968) and  $\Delta H_f^\circ(\text{Ba}^{2+})(g) = 1660 \text{ kJ mol}^{-1}$  (from Rossini, 1968) :  $\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) = -792 \text{ kJ mol}^{-1}$  or

$$\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) - \Delta H_f^\circ(\text{BaPtCl}_6)(c) - \frac{1}{2}RT \quad (74)$$

$1047 \text{ kJ mol}^{-1}$ . (75)

if  $\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) = -527 \text{ kJ mol}^{-1}$  (Goldberg & Hepler 1968) and  $\Delta H_f^\circ(\text{Ba}^{2+})(g) = 1660 \text{ kJ mol}^{-1}$  (from Rossini, 1968) we have

$$\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) - \Delta H_f^\circ(\text{Ag}_2\text{PtCl}_6)(c) \quad (76)$$

$1773 \text{ kJ mol}^{-1}$ . (77)

the  $\text{PtCl}_6^{2-}$  is measured by the process



$$\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) - \Delta H_f^\circ(\text{PtCl}_6^{2-})(c) \quad (78)$$

$1773 \text{ kJ mol}^{-1}$  (Jenkins & Morris 1976a) and  $1773 \text{ kJ mol}^{-1}$  (Jenkins & Morris 1976a) and  $1773 \text{ kJ mol}^{-1}$  (Jenkins & Morris 1976a), we find

$$\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) = -757 \text{ kJ mol}^{-1} \quad (79)$$

$\Delta H_f^\circ(\text{PtCl}_6^{2-})(g) = -757 \text{ kJ mol}^{-1}$  derived from our value  $-757 \text{ kJ mol}^{-1}$  from the value  $-757 \text{ kJ mol}^{-1}$  (Jenkins & Morris 1976a), the two values quoted for

## 5. FUTURE EXTENSIONS

Using the method outlined here we now find ourselves in a position to evaluate the lattice energies of salts possessing spherical ions of transition metals and propose to embark on such a study. Initially we shall consider salts having the antifuorite structure where considerable crystal data, although a paucity of thermochemical data is available.

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## REFERENCES

- Baughan, E. C. 1959a *Trans. Faraday Soc.* **55**, 736-752.  
 Baughan, E. C. 1959b *Trans. Faraday Soc.* **55**, 2025-2029.  
 Cotton, F. A. & Harris, C. B. 1967 *Inorg. Chem.* **6**, 376.  
 Coulter, L. V., Pitzer, K. S. & Latimer, W. M. 1940 *J. Am. Chem. Soc.* **62**, 2845-2851.  
 Cubicciotti, D. 1959 *J. Chem. Phys.* **31**, 1646-1651.  
 Cubicciotti, D. 1961a *J. Chem. Phys.* **34**, 2189.  
 Cubicciotti, D. 1961b *J. Phys. Chem.* **65**, 1058-1059.  
 De Jonge, R. M. 1976 *J. Inorg. Nucl. Chem.* **38**, 1821-1826.  
 Goldberg, R. N. & Hepler, L. G. 1968 *Chem. Rev.* **68**, 229-252.  
 Hartley, F. R. 1972 *Nature Phys. Sci.* **236**, 75-77.  
 Herzfeld, K. F. & Woolf, K. L. 1928 *Ann. Physik.* **78**, 35-45.  
 Herzig, P., Jenkins, H. D. B. & Neckel, A. 1976 *J. Phys. Chem.* **80**, 1608-1611.  
 Huggins, M. L. 1937 *J. Chem. Phys.* **5**, 143-148.  
 Huggins, M. L. & Mayer, J. E. 1933 *J. Chem. Phys.* **1**, 643-648.  
 Jaswal, S. S. & Sharma, T. P. 1973 *J. Phys. Chem. Solids* **34**, 509-513.  
 Jenkins, H. D. B. 1977 *J. Phys. Chem.* (in the Press).  
 Jenkins, H. D. B. & Morris, D. F. C. 1976a *Molec. Phys.* **32**, 231-235.  
 Jenkins, H. D. B. & Morris, D. F. C. 1976b *Molec. Phys.* (in the Press).  
 Jenkins, H. D. B. & Pratt, K. F. 1976a *J. Inorg. Nucl. Chem.* **38**, 1775-1781.  
 Jenkins, H. D. B. & Pratt, K. F. 1976b Repulsion energy and 'basic' radii for ions having spherical symmetry. *Res. Rep. Supp.* no. 1.  
 Jenkins, H. D. B., Pratt, K. F., Smith, B. T. & Waddington, T. C. 1976 *J. Inorg. Nucl. Chem.* **38**, 371-377.  
 Jenkins, H. D. B. & Waddington, T. C. 1975 *Chem. Phys. Lett.* **31**, 368-371.  
 Jenkins, H. D. B. & Waddington, T. C. 1977 *Adv. Inorg. Chem. Radiochem.* (in preparation).  
 Kubo, M. & Nakamura, T. 1966 *Adv. Inorg. Chem. Radiochem.* **8**, 256-282.  
 Lister, M. W., Nyburg, S. C. & Poyntz, R. B. 1974 *J. Chem. Soc. Faraday I*, **70**, 685-693.  
 Mayer, J. E. 1933 *J. Chem. Phys.* **1**, 270-279.  
 Michael, A. J. 1969 *J. Chem. Phys.* **51**, 5730-5731.  
 Morris, D. F. C. & Short, E. L. 1969 *Nature, Lond.* **224**, 950-952.  
 Pauling, L. 1927 *Proc. Roy. Soc. A* **114**, 181-211.  
 Pirene, J. & Kartheiser, E. 1964 *Physica* **30**, 2005-2018.  
 Rossini, F. D., Wagman, D. D., Levine, S. & Jaffe, I. 1952 Selected values of chemical thermodynamic properties. *N.B.S. Circular*, no. 500. Washington D.C., USA.  
 Shidlovskii, A. A. & Valkina, K. V. 1961 *Russian J. Phys. Chem.* **35**, 142-143.  
 Teesman, J. R., Kahn, A. H. & Shockley, W. H. 1953 *Phys. Rev.* **92**, 890-895.  
 Tosi, M. P. 1963 *J. Phys. Chem. Solids* **24**, 965-967.

- Tosi, M. P. 1964 *Solid State Phys.* 16, 1-120.  
Tsai, K. R. 1962 *Univ. Amoiensis Acta Sci. Nat.* 9, (1), 1-9.  
Tsai, K. R. 1964 *Sci. Sinica* 13, 47-59.  
Waddington, T. C. 1959 *Adv. Inorg. Chem. Radiochem.* 1, 157-221.  
Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M. & Schumm, R. H.  
1968 Selected values of chemical thermodynamic properties. *Tech. Note*, no. 270.  
N.B.S. Washington, D.C., USA.  
Wyckoff, R. W. G. 1965 *Crystal Structures*, 2nd ed. New York: Interscience.

K. F. PRATT

(1), 1-9.

*Chem.* 1, 157-221.

ow, I., Bailey, S. M. & Schumm, R. H.  
dynamic properties. *Tech. Note*, no. 270.

New York: Interscience.

**Minimisation Equations Applied to the Calculation of the Lattice  
Energies of Alkali-metal Cyanides having Cubic Structures**

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# Minimisation Equations Applied to the Calculation of the Lattice Energies of Alkali-metal Cyanides having Cubic Structures

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We report results from our improved<sup>1</sup> minimisation technique centred around the Huggins and Mayer<sup>2</sup> expression for the repulsion energy as incorporated into the equation for the total lattice energy for salts possessing complex ions, as applied to the case of the cubic cyanides of the alkali metals. The method used is outlined briefly in the full text. Scheme 1 gives the results from this latest calculation, which involves computation of the "basic" radius for the CN<sup>-</sup> ion and the lattice potential energies of the alkali-metal cyanides. Wyckoff<sup>3</sup> and Donnay<sup>4</sup> cite slightly different  $a_0$  values for the cyanides; results for both are given since the earlier work used the former parameters.

Scheme 2 reports the results obtained by using the form of repulsion energy,  $U_R$ , derived by Jenkins

from considerations<sup>3,4</sup> involving direct minimisation of the total lattice potential energy when  $U_R$  takes the form:  $A \exp(-a/\rho)$ . This approach effectively considers only nearest-neighbour interactions to a given ion. The results from Schemes 1 and 2 are similar, reflecting the fact that, at least for the case of the cubic cyanides the nearest-neighbour approximation is a reasonably satisfactory one.

Schemes 3 and 4 report the results for  $\bar{r}_{CN^-}$  and  $U_{POT}(MCN)$  from our three earlier studies<sup>6-8</sup> and the following points are noted:

(i) the "basic" radius of the CN<sup>-</sup> ion used in our first studies<sup>6,7</sup> ( $\bar{r}_{CN^-} = 1.57 \text{ \AA}$ ) is validated by the later study ( $\bar{r}_{CN^-} = 1.58 \text{ \AA}$ ),<sup>8</sup> and the fact that the present method<sup>1,2</sup> generates radii ( $\bar{r}_{CN^-} = 1.56 \text{ \AA}$ ) close to these indicates its reliability.

## Scheme 1 Jenkins and Pratt Calculation<sup>1,2</sup>

Optimised "basic" radii

Directly Minimised Huggins and Mayer<sup>2</sup> Equation  $\rho = 0.345 \text{ \AA}$ 

	CUBIC				
	NaCN	KCN	RbCN	CsCN	
$U_{POT}$ (Wyckoff <sup>3</sup> )	736	672	647	618	$\text{kJ mol}^{-1}$
$\bar{r}_{CN^-}$	1.56	1.55	1.55	1.53	$\text{\AA}$
$U_{POT}$ (Donnay <sup>4</sup> )	738*	674*	648*	612*	$\text{kJ mol}^{-1}$
$\bar{r}_{CN^-}$	1.56	1.55	1.56	1.55	$\text{\AA}$
$U_{dd}$ and $U_{qd}$ recalculated. Averaged $\bar{r}_{CN^-} = 1.56 \text{ \AA}$					

## Scheme 2 Jenkins and Pratt Calculation

Ladd and Lee Equation<sup>1,2</sup>

$$\left( \frac{\partial M_{ELEC}}{\partial a} \right)_{a=a_0} = 0 \quad U_R = A \exp(-a/\rho)$$

Directly Minimised Born Mayer Equation  
 $\rho = 0.348 \text{ \AA}$ 

	CUBIC				
	NaCN	KCN	RbCN	CsCN	
$U_{POT}$ (Wyckoff <sup>3</sup> )	730	670	646	616	$\text{kJ mol}^{-1}$
$U_{POT}$ (Donnay <sup>4</sup> )	732*	672*	645*	610*	$\text{kJ mol}^{-1}$
$U_{dd}$ and $U_{qd}$ recalculated.					
$U_R = \frac{2\rho}{\sqrt{3}a_0} [U_{ELEC} + 8U_{dd} + 8U_{qd}]$ for CsCl type structure (CsCN)					
$U_R = \frac{2\rho}{a_0} [U_{ELEC} + 6U_{dd} + 8U_{qd}]$ for NaCl type structure (NaCN, KCN, RbCN)					

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<sup>3,4</sup> involving direct minimisation potential energy when  $U_R$  takes  $-a/\rho$ . This approach effectively rest-neighbour interactions to a ults from Schemes 1 and 2 are re fact that, at least for the case of the nearest-neighbour approxima-satisfactory one.

4 report the results for  $\bar{r}_{CN^-}$  and our three earlier studies<sup>6-8</sup> and s are noted:  
radius of the  $CN^-$  ion used in our  $N^- = 1.57\text{\AA}$ ) is validated by the  $= 1.58\text{\AA}$ ),<sup>8</sup> and the fact that the generates radii ( $\bar{r}_{CN^-} = 1.56\text{\AA}$ ) ates its reliability.

Scheme 3 Jenkins and Pratt Calculation.<sup>6</sup>  
Jenkins, Pratt and Waddington Calculation.<sup>7</sup>  
Extended Huggins and Mayer Equation.

CUBIC					
	NaCN	KCN	RbCN	CsCN	
$U_{POT}$	729	664	638	601	$\text{kJ mol}^{-1}$
Huggins radius of $CN^-$ ion taken as $1.57\text{\AA}$ $U_{dd}$ calculated. $U_{qd}$ ignored.					

Scheme 4 Jenkins and Morris Correlation.<sup>9</sup>  
Method 2 of Morris.<sup>11</sup>  
Empirical Correlation.

CUBIC		
	NaCN	KCN
$U_{POT}$	755*	682*
$\text{kJ mol}^{-1}$		
Hydration enthalpy radius plot. $CN^-$ electron density radius = $1.77\text{\AA}$ . Huggins radius of $CN^-$ = $1.58\text{\AA}$ .		

Scheme 5 Other Literature Values  
Ladd,<sup>15</sup> Morris,<sup>16</sup> and Waddington<sup>17</sup>

CUBIC					
	NaCN	KCN	RbCN	CsCN	
$U_{POT}$	728	674	640	611	Ladd and Lee Equation <sup>15</sup>
$(\text{kJ mol}^{-1})$	741*	665*	—	—	Lyotropic Number <sup>16</sup>
	728*	661*	632*	582*	Born Mayer Equation <sup>17</sup>
	712	655	629	596	Term by Term <sup>17</sup>
	739	671	641	601	Average of *values in Frames.

Scheme 5 compares other literature values for the cubic salts considered here and gives the average of the values obtained for  $U_{POT}$  derived by considering the most recent studies which involve different approaches (Ladd and Lee equation, Lyotropic number, Hydration enthalpy – radius correlation, Simple Born Mayer Equation and the Latest Direct Minimisation). The agreement between the  $U_{POT}$  values and the assigned radius for  $CN^-$  tends to support our new approach.

References: 17

Table I: Lattice energies of alkali-metal cyanides. Direct minimisation: Huggins and Mayer Repulsion.

Table II: Lattice energies of alkali-metal cyanides. Direct minimisation: Born Mayer Repulsion.

Table III: Lattice energies of alkali-metal cyanides. Extended Huggins and Mayer Calculation, and Reciprocal Radius–Hydration Enthalpy Plot.

Table IV: Lattice energies of alkali-metal cyanides. Literature Values.

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References cited in this synopsis:

- <sup>1</sup> H. D. B. Jenkins and K. F. Pratt, *Proc. Roy. Soc.*, submitted for publication.
- <sup>2</sup> H. D. B. Jenkins and K. F. Pratt, *Repulsion Energy and "Basic" Radil for Ions having Spherical Symmetry. Research Report supplement No. 1* (1976).
- <sup>3</sup> H. D. B. Jenkins and T. C. Waddington, *Chem. Phys. Letters*, 1975, 31, 369.
- <sup>4</sup> H. D. B. Jenkins, *JCS Faraday II*, 1976, 72, 1569.
- <sup>5</sup> M. L. Huggins and J. E. Mayer, *J. Chem. Phys.*, 1933, 1, 643.
- <sup>6</sup> H. D. B. Jenkins and K. F. Pratt, *J. Inorg. Nuclear Chem.*, 1976, 38, 1775.
- <sup>7</sup> H. D. B. Jenkins, K. F. Pratt, and T. C. Waddington, *J. Inorg. Nuclear Chem.*, in proof.
- <sup>8</sup> H. D. B. Jenkins and D. F. C. Morris, *Mol. Phys.*, in the press.
- <sup>9</sup> R. W. G. Wyckoff, "Crystal Structures", Interscience, 2nd Edn., New York, 1965.
- <sup>10</sup> J. D. H. Donnay and H. M. Ondik, "Crystal Structures", Vol III, 3rd. Edn.N.S.R.D.S.–J.C.P.D.S., U.S.A., 1973.
- <sup>11</sup> D. F. C. Morris, *Structure and Bonding*, 1968, 4, 63.
- <sup>12</sup> M. F. C. Ladd and W. H. Lee, *Trans. Faraday Soc.*, 1958, 54, 34.
- <sup>13</sup> M. F. C. Ladd, *Trans. Faraday Soc.*, 1969, 65, 2712.
- <sup>14</sup> D. F. C. Morris, *Acta Cryst.*, 1961, 14, 547.
- <sup>15</sup> T. C. Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, 1, 159.



# THERMOCHEMISTRY OF AZIDE SALTS AND THE AZIDE ION USING DIRECT MINIMISATION EQUATIONS TO OBTAIN THE LATTICE ENERGY OF THE UNIVALENT AZIDE SALTS

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**Abstract**—The opportunity to test a new equation for the computation of the lattice energy and at the same time examine a disparity in the literature data for the enthalpy of formation of the azide ion,  $\Delta H_f^\circ(\text{N}_3^-)(\text{g})$  was the motivation for this study. The results confirm our earlier calculation and show the new equation to be reliable. Thermodynamic data produced in the study take values:

$$\Delta H_f^\circ(\text{N}_3^-)(\text{g}) = 144 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{ion}}^\circ(\text{N}_3^-)(\text{g}) = -315 \text{ kJ mol}^{-1}$$

or

$$\Delta H_{\text{ion}}^\circ(\text{N}_3^-)(\text{g}) = -295 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{NaN}_3) = 732 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{KN}_3) = 659 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{RbN}_3) = 637 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{CsN}_3) = 612 \text{ kJ mol}^{-1}$$

$$U_{\text{pot}}(\text{TlN}_3) = 689 \text{ kJ mol}^{-1}$$

The lattice energies of azides whose enthalpies of formation are documented have been calculated as well as the enthalpy of formation of the azide radical.

## INTRODUCTION

This study of the lattice energy and related thermochemical data of the univalent metal azides seems, to us, timely for at least four reasons: (i) Our previous extended term by term calculations[1], which parameterised the thermodynamic data as a function of the charge on the terminal atoms of the  $\text{N}_3^-$  ion,  $q_N$ , gave a value for  $\Delta H_f^\circ(\text{N}_3^-)(\text{g})$  of  $142 \text{ kJ mol}^{-1}$ . This value is some  $40 \text{ kJ mol}^{-1}$  less than the value quoted ( $180 \text{ kJ mol}^{-1}$ ) as having an error of only  $4 \text{ kJ mol}^{-1}$  in the most recent thermochemical tabulations[2, 3], although it agreed with some work carried out fifteen years ago[4] ( $146 \text{ kJ mol}^{-1}$ ). This disparity needs investigation.

A possible cause of the disparity is the fact that an ellipsoid model was taken for the  $\text{N}_3^-$  ion whereas in a later study of the  $\text{HF}_2^-$  ion[5] such a model was shown to be inappropriate. The opportunity of using the new

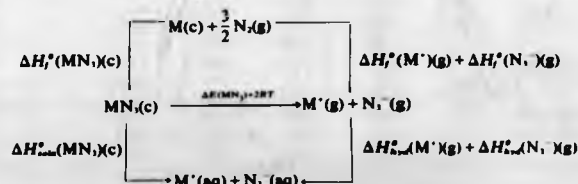
equation avoids the issue of choosing a model for the ion and we carry out such a calculation with the new crystal structure data as well as repeating calculations based on an ellipsoid model for comparison.

(ii) The crystal structure of the two azides  $\text{KN}_3$  and  $\text{RbN}_3$ , treated in the former study[1], have been redetermined recently[6].

(iii) Our study can be extended to include  $\text{CsN}_3$  and  $\text{TlN}_3$ , since crystal structures are now available for these salts[4].

(iv) We have recently developed[7, 8] an alternative approach to the calculation of the repulsion energy for crystal lattices and a study of the azides provides direct comparison to our previous calculations and a means of monitoring the results of the new approach.

Using the thermochemical cycle:





as in the previous work, we can calculate  $\Delta H_f^\circ(N_3^-)(g)$  as a function of charge,  $q_N$ , and do so, assigning a value for this parameter on the basis of the intersection point in Fig. 1. The enthalpy of hydration,  $\Delta H_{hyd}^\circ(N_3^-)(g)$  not treated previously, is also considered for these salts whose enthalpies of solution are known[7].

The equations associated with the cycle take the usual form:

$$\Delta E(MN_i) + 2RT = \Delta H_f^\circ(M^+)(g) + \Delta H_f^\circ(N_3^-)(g) - \Delta H_f^\circ(MN_i)(c) \quad (1)$$

$$U_{POT}(MN_i) = \Delta E(MN_i) + 2RT = \sum_{i=0}^2 D_i q_N^i \quad (2)$$

where  $\Delta E(MN_i)$  is the total internal energy change in the lattice energy step and  $U_{POT}(MN_i)$  is the total lattice energy and  $D_i$  ( $i = 0, 1, 2$ ) are the coefficients expressing the charge dependence. The thermodynamic parameters of direct interest in this study can be written:

$$\begin{aligned} \Delta H_f^\circ(N_3^-)(g) &= U_{POT}(MN_i) + \Delta H_f^\circ(MN_i)(c) \\ -\Delta H_f^\circ(M^+)(g) &= \sum_{i=0}^2 E_i q_N^i \end{aligned} \quad (3)$$

and

$$\begin{aligned} \Delta H_{hyd}^\circ(N_3^-)(g) &= \Delta H_{hyd}^\circ(MN_i)(c) - U_{POT}(MN_i) \\ -\Delta H_{hyd}^\circ(M^+)(g) &= \sum_{i=0}^2 F_i q_N^i \end{aligned} \quad (4)$$

and can be plotted as functions of the charge, where  $E_i$  and  $F_i$  ( $i = 0, 1, 2$ ) are the coefficients determined in this study.

The Madelung parameter,  $M_{ELEC}$ , (based on the cell parameter,  $a_0$ ), related to  $U_{ELEC}$  by the equation:

$$U_{ELEC} = KM_{ELEC}/a_0 \quad (5)$$

where  $K$  is the conversion factor from  $e^2/\text{\AA}$  to  $\text{kJ mole}^{-1}$  and  $M_{ELEC}$  can be expanded in the form:

$$M_{ELEC} = \alpha_0 + \left( \sum_{i=1}^{\infty} \alpha_i \left( \frac{d}{a_0} \right)^i \right) q_N + \left( \sum_{i=1}^{\infty} \beta_i \left( \frac{d}{a_0} \right)^i \right) q_N^2 \quad (6)$$

The lattice potential energy,  $U_{POT}(MN_i)$  for the univalent azides is then given by [8]:

$$\begin{aligned} U_{POT}(MN_i) &= U_{ELEC} + U_{d1} + U_{d2} \\ &= \frac{\rho}{a} \left[ U_{ELEC} + 6U_{d1} + 8U_{d2} \right. \\ &\quad \left. - K \left( \frac{\partial M_{ELEC}}{\partial a} \right)_{a=a_0} \right] \end{aligned} \quad (7)$$

where  $U_{d1}$  and  $U_{d2}$  are the dipole and quadrupole dipole dispersion energy terms and  $\rho$  is the repulsion exponent (taken as 0.345 Å) when the repulsion energy,  $U_R$ , is written in the form:

$$U_R = B \exp(-a/\rho) \quad (8)$$

and  $a$  is taken to be the shortest cation anion distance in the salt, after the method of Born and Mayer [10].

Since:

$$\begin{aligned} K \left( \frac{\partial M_{ELEC}}{\partial a} \right)_{a=a_0} &= -\frac{K}{a_0} \left[ \left( \sum_{i=1}^{\infty} i \alpha_i \left( \frac{d}{a_0} \right)^{i-1} \right) q_N \right. \\ &\quad \left. + \left( \sum_{i=1}^{\infty} i \beta_i \left( \frac{d}{a_0} \right)^{i-1} \right) q_N^2 \right] = \sum_{i=1}^{\infty} G_i q_N^i \end{aligned} \quad (9)$$

then  $U_R$  takes the parametric form:

$$U_R = \frac{\rho}{a} \sum_{i=0}^2 H_i q_N^i = \sum_{i=0}^2 J_i q_N^i \quad (10)$$

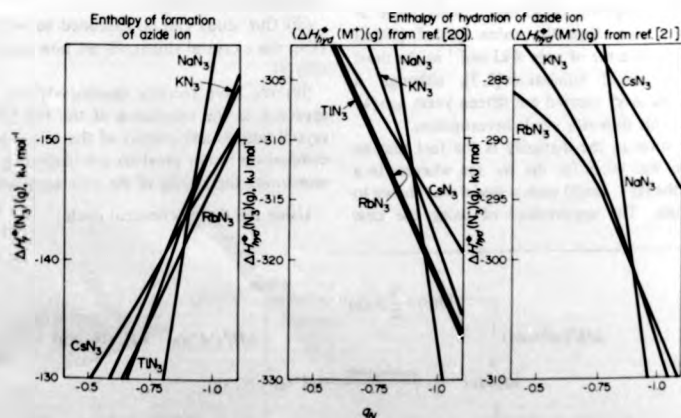


Fig. 1.

here  $K$  is the conversion factor from  $\text{e}^2 \text{\AA}^{-1}$  to  $\text{kJ mole}^{-1}$ , and  $M_{\text{ELC}}$  can be expanded in the form:

$$M_{\text{ELC}} = \alpha_0 + \left( \sum_{i=1}^n \alpha_i \left( \frac{d}{a_0} \right)^i \right) q_v + \left( \sum_{i=1}^n \beta_i \left( \frac{d}{a_0} \right)^i \right) q_v^2 \quad (6)$$

The lattice potential energy,  $U_{\text{POT}}(\text{MN}_3)$  for the trivalent azides is then given by [8]:

$$U_{\text{POT}}(\text{MN}_3) = U_{\text{ELC}} + U_{\text{dip}} + U_{\text{quad}} - \frac{\rho}{a} \left[ U_{\text{ELC}} + 6U_{\text{dip}} + 8U_{\text{quad}} - K \left( \frac{\partial M_{\text{ELC}}}{\partial a} \right)_{a=a_0} \right] \quad (7)$$

here  $U_{\text{dip}}$  and  $U_{\text{quad}}$  are the dipole and quadrupole dipole dispersion energy terms and  $\rho$  is the repulsion exponent taken as 0.345  $\text{\AA}$  when the repulsion energy,  $U_R$ , is written in the form:

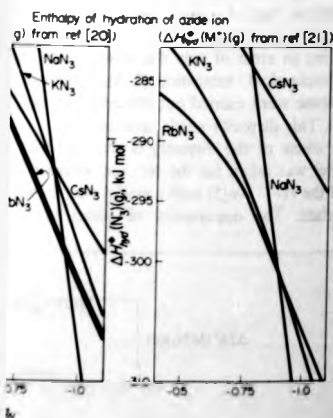
$$U_R = B \exp(-a/\rho) \quad (8)$$

and  $a$  is taken to be the shortest cation-anion distance in the salt, after the method of Born and Mayer [10]. Since:

$$K \left( \frac{\partial M_{\text{ELC}}}{\partial a} \right)_{a=a_0} = - \frac{K}{a_0} \left[ \left( \sum_{i=1}^n i \alpha_i \left( \frac{d}{a_0} \right)^{i-1} \right) q_v + \left( \sum_{i=1}^n i \beta_i \left( \frac{d}{a_0} \right)^{i-1} \right) q_v^2 \right] = \sum_{i=1}^n G_i q_v^i \quad (9)$$

and  $U_R$  takes the parametric form:

$$U_R = \frac{\rho}{a} \sum_{i=0}^n H_i q_v^i = \sum_{i=0}^n J_i q_v^i \quad (10)$$



where:

$$H_0 = \left[ \frac{K\alpha_0}{a_0} + 6U_{\text{dip}} + 8U_{\text{quad}} \right] \quad (11)$$

$$H_i (i \neq 0) = \left[ \frac{K\alpha_i}{a_0} + G_i \right] \quad (12)$$

## 2. CALCULATIONS

The crystal structure of  $\text{NaN}_3$  has not been revised since the previous work [1]. Sodium azide has a rhom-

bohedral unimolecular unit cell with  $a = 5.488 \text{ \AA}$  and  $\alpha = 38^\circ 43'$ . The structures of potassium, rubidium, cesium and thallium azides [6] have been determined recently. All have tetragonal symmetry and tetramolecular cells. The cell dimensions are  $a = 6.1129 \text{ \AA}$ ,  $c = 7.0943 \text{ \AA}$ ;  $a = 6.3098 \text{ \AA}$ ,  $c = 7.5188 \text{ \AA}$ ;  $a = 6.5412 \text{ \AA}$ ,  $c = 8.0908 \text{ \AA}$  and  $a = 6.208 \text{ \AA}$ ,  $c = 7.355 \text{ \AA}$  respectively.

In Table 1, the intermediate results are given for various parameters.  $M$  is the Madelung constant (based on  $d$ , the

Table 1. Parameterisation of equations for univalent azides  $\text{MN}_3$  ( $M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$  and  $\text{Tl}$ )

		NaN <sub>3</sub>	KN <sub>3</sub>	RbN <sub>3</sub>	CsN <sub>3</sub>	TlN <sub>3</sub>	Notes
$M$	$\epsilon_0$	0.516995	0.573325	0.550108	0.527846	0.554392	
	$\epsilon_1$	1.754819	1.980076	1.986364	1.993859	1.985069	
	$\epsilon_2$	3.435693	3.530855	3.525939	3.522332	3.526751	
	$d(\text{\AA})$	1.1407	1.1800	1.1690	1.1656	1.1589	
	$A_0$	629.6	675.0	653.8	629.1	664.6	
$U_{\text{dip}}$ (kJ mol <sup>-1</sup> )	$A_1$	2137.2	2331.3	2360.7	2376.5	2379.7	
	$A_2$	4184.3	4157.1	4190.4	4198.3	4227.9	
	$B_1$	-2435.8	-2354.7	-2376.9	-2383.9	-2397.6	
	$B_2$	-4262.6	-4120.8	-4159.6	-4171.8	-4195.9	
	$C_0$	629.6	675.0	653.8	629.1	664.6	
$U_{\text{ELC}}$ (kJ mol <sup>-1</sup> )	$C_1$	-298.6	-23.5	-16.2	-7.3	-17.9	
	$C_2$	-78.3	36.3	30.8	26.5	32.0	
	$U_{\text{dip}}^{\text{calc}}$	0.2	1.6	3.0	5.8	33.2	$\alpha_{\text{N}_3} = 4.44 \text{ \AA}^3$
	$U_{\text{ELC}}^{\text{calc}}$	18.6	12.6	9.6	6.9	10.8	$\epsilon_{\text{N}_3} = 13.1 \times 10^{-2} \text{ erg molecule}^{-1}$
	$U_{\text{dip}}^{\text{calc}}$	4.6	15.6	20.0	25.4	75.2	
$U_{\text{dip}}$ (kJ mol <sup>-1</sup> )	$U_{\text{dip}}^{\text{calc}}$	23.4	29.8	32.6	38.1	119.2	
	$U_{\text{dip}}^{\text{calc}}$	23.9	31.0	33.0	—	—	Previous work [1]
	$U_{\text{dip}}^{\text{calc}}$	0.0	0.1	0.2	0.6	4.9	
	$U_{\text{dip}}^{\text{calc}}$	1.7	1.0	0.7	0.4	0.8	
	$U_{\text{dip}}^{\text{calc}}$	0.7	2.7	3.9	5.7	22.3	
$U_R$ (kJ mol <sup>-1</sup> )	$U_{\text{dip}}^{\text{calc}}$	2.4	3.8	4.8	6.7	28.0	
	$U_{\text{dip}}^{\text{calc}}$	25.8	33.6	37.4	44.8	147.2	
	$U_{\text{dip}}^{\text{calc}}$	64.7	73.5	67.3	57.0	81.9	Ellipsoid model
	$U_{\text{dip}}^{\text{calc}}$	63.5	79.5	69.1	—	—	Previous work [1]
	$U_{\text{dip}}^{\text{calc}}$	—	—	—	—	—	
$U_R$ (kJ mol <sup>-1</sup> )	$H_0$	789.2	884.2	887.8	911.3	1603.8	Direct minimisation eqn (9)
	$H_1$	205.1	17.8	21.0	32.1	19.9	
	$H_2$	186.0	196.4	163.8	139.5	170.8	
	$G_1$	503.7	-41.3	-37.2	-39.4	-37.8	Direct minimisation, $K \left( \frac{\partial M_{\text{ELC}}}{\partial a} \right)_{a=a_0}$ eqn (11)
	$G_2$	264.3	-160.1	-133.0	-112.9	-138.8	anion-cation distance This work
$U_{\text{POT}}$ (kJ mol <sup>-1</sup> )	$a$	3.2923	3.5338	3.6724	3.8455	3.6077	
	$J_0$	82.7	86.3	83.4	81.8	153.4	
	$J_1$	-84.1	1.7	2.0	2.9	1.9	
	$J_2$	-35.9	19.2	15.4	12.5	16.3	
	$U_R$	129	100	94	89	165	based on $q_v = -0.9$
$U_{\text{POT}}$ (kJ mol <sup>-1</sup> )	$K_0$	572.7	622.3	607.8	592.1	658.4	
	$K_1$	-214.8	-25.2	-18.2	-10.2	-19.8	
	$K_2$	-42.4	17.1	15.4	14.0	15.7	
	$U_{\text{POT}}(\text{MN}_3)$	732	659	637	612	689	
	$\Delta H_f^0(\text{MN}_3)(\text{c})$	21.25	-1.38	-0.29	-9.92	233.4	Ref. [4]
$\Delta H_f^0(\text{M}^+)(\text{g})$	$\Delta H_f^0(\text{M}^+)(\text{g})$	609.84	514.2	494.9	458.6	777.7*	Refs [3, 31]
	$E_0$	-15.9	106.7	112.6	123.6	114.1	
	$E_1$	-214.8	-25.2	-18.2	-10.2	-19.8	
	$E_2$	-42.4	17.1	15.4	14.0	15.7	
	$\Delta H_f^0(\text{N}_3)(\text{g})$	13.26	24.35	28.03	36.40	46.57	Ref. [9]
$\Delta H_f^0(\text{MN}_3)(\text{c})$	$\Delta H_f^0(\text{MN}_3)(\text{c})$	-405.9	-321.9	-300.8	-276.5	-326.0*	Ref. [20] values
	$\Delta H_f^0(\text{M}^+)(\text{g})$	-417.1	-333.0	-306.7	-289.1	—	Ref. [21] values
	$\Delta H_f^0(\text{M}^+)(\text{g})$	-153.5	-276.0	-279.0	-274.2	-285.8	calculated using $\Delta H_f^0(\text{M}^+)(\text{g})$ from Ref. [20]
	$\Delta H_f^0(\text{N}_3)(\text{g})$	214.8	25.2	18.2	10.2	19.8	
	$\Delta H_f^0(\text{N}_3)(\text{g})$	42.4	-17.1	-15.4	-14.0	-15.7	calculated using $\Delta H_f^0(\text{M}^+)(\text{g})$ from Ref. [21]

shortest distance in the salt, N-N) for the process:  $MN_3(c) \rightarrow M^+(g) + N^{q_N}(g) + 2N^{q_N}(g)$ , for which the energy change is  $U_M$ , where  $q_N$  is the charge on the central atom of the  $N_3^-$  ion and takes the form:

$$M = \sum_i \epsilon_i q_N^i \quad (13)$$

$U_M$  can be written as a function of  $q_N$ :

$$U_M = \sum_i A_i q_N^i \quad (14)$$

$M$  was computed using the method of Bertaut[11] using a truncation procedure developed by Jenkins[12, 13]. The self energy of the ion,  $U_{SE}$ , corresponding to the process:  $N^{q_N}(g) + 2N^{q_N}(g) \rightarrow N_3^-(g)$  was calculated as a function of  $q_N$ :

$$U_{SE} = \sum_i B_i q_N^i \quad (15)$$

$U_{ELC}$  coefficients,  $C_i$  ( $i = 0, 1, 2$ ) are quoted in Table 1.

$$U_{ELC} = U_M + U_{SE} = A_0 + \sum_i (A_i + B_i) q_N^i = \sum_i C_i q_N^i \quad (16)$$

In the previous work, the dispersion energy,  $U_D$ , included only dipole dipole interactions,  $U_{dd}$ . This was a reasonable approximation in the case of the alkali metal azides but, not however, for thallium azide where the dipole quadrupole term is large. In the present study,  $U_{qd}$  is calculated for all the salts, using the equations:

$$U_D = [U_{dd} + U_{qd}] = [(U_{dd}^+ + U_{dd}^- + U_{dd}^0) + (U_{qd}^+ + U_{qd}^- + U_{qd}^0)] \quad (17)$$

and

$$U_D = \left[ c \cdot S_0^{++} + \frac{1}{2} (c \cdot S_0^{+-} + c \cdot S_0^{-+}) \right] + \left[ d \cdot S_0^{++} + \frac{1}{2} (d \cdot S_0^{+-} + d \cdot S_0^{-+}) \right] \quad (18)$$

where:

$$C_0 = \frac{2}{3} \epsilon^2 \frac{Q_{im}^2 Q_{jm}^2}{(e_i + e_j)} \quad (19)$$

$$d_0 = \frac{3}{2} c_0 \left( \frac{Q_{im}^2}{P_i} + \frac{Q_{jm}^2}{P_j} \right) \quad (20)$$

$$Q_{im}^2 = \frac{3 \alpha_i e_i}{2 \epsilon^2} \quad (21)$$

where  $\epsilon$  is the electronic charge,  $e_i$  is the characteristic energy of the ion,  $\alpha_i$  is the polarisability of the ion and  $p_i$  is the "electron number" of the ion, and

$$S_0^{++} = \sum_i (R_{MM_i})^{-4} \quad (22)$$

$$S_0^{+-} = \sum_i (R_{NN_i})^{-4} \quad (23)$$

$$S_0^{-+} = \sum_i (R_{MM_i})^{-4} \quad (24)$$

where  $N_i$  represents the charge on the central nitrogen atom of the azide ion, the summations being performed exhaustively.

Data is available for the polarisability,  $\alpha$ , of the  $N_3^-$  ion and the value  $4.44 \text{ \AA}^3$ , the average of the anisotropic values quoted by Frech and Decius[14] was assumed. This value is close to  $\alpha_{B_3} = 4.81 \text{ \AA}^3$  which was used for the azide ion in the previous calculations[1].

The characteristic energy of the  $N_3^-$  ion is estimated as 90% of the second ionisation potential of the N. ion as calculated by Archibald and Sabin[15], which gives the value  $\epsilon_i = 13.1 \times 10^{-12} \text{ erg molecule}^{-1}$ . This is close to the value of  $\epsilon_i$  for the  $Br^-$  ion as used in our previous study ( $14.0 \times 10^{-12} \text{ erg molecule}^{-1}$ ).

The "electron numbers",  $p_i$ , were taken as 8 for all ions except  $Tl^+$ , where a value of 11 was used[16]. The values of  $U_{dd}$ ,  $U_{qd}$  and the total  $U_D$  are given in Table 1.

Previously, the repulsion energy,  $U_R$ , of the salts was calculated by assuming that the azide ion could be represented by an ellipsoid of revolution about the major axis.  $U_R$  was calculated using the Huggins and Mayer[17-19] approach. The ellipsoid axes used had lengths 1.764 and 2.545  $\text{\AA}$ . This model has been employed with the newer crystal data and the results are given in Table 1.

$U_R$ , as calculated by the new equation, in the form of the final term of eqn (7) is given in Table 1 and the coefficients of  $M_{ELC}$  in eqn (6) are listed in Table 2 so that the value of the  $K(\partial M_{ELC}/\partial a)_d$  term can be studied in the discussion section of this paper. The coefficients  $J$  give the quadratic dependence of the repulsion energy term, calculated taking  $\rho = 0.345 \text{ \AA}$  and  $a$  as the shortest metal-azide distance. The coefficients  $C_i$  for  $U_{ELC}$  as generated from the expansion coefficients  $a_i$  and  $\beta_i$  from eqn (6) are given in Table 2 for comparison with those in Table 1.

The coefficients,  $K_i$  ( $i = 0, 1, 2$ ) of the total lattice energy are calculated using the equation:

$$U_{TOT}(MN_3) = [C_0 - J_0 + U_D] + \sum_i (C_i - J_i) q_N^i = \sum_i K_i q_N^i \quad (25)$$

and are given in Table 1.

### 3 RESULTS

Figure 1 displays a plot of  $\Delta H_f^\circ(N_3^-(g))$  vs  $q_N$  from which an average intersection corresponding to:

$$\Delta H_f^\circ(N_3^-(g)) = 144 \text{ kJ mol}^{-1} \quad (26)$$

$$q_N = -0.91. \quad (27)$$

The figure also shows plots of  $\Delta H_f^\circ(N_3^-(g))$  vs  $q_N$  using data for  $\Delta H_f^\circ(M^+(g))$  from Halliwell and Nyburg's

$$S_N = \sum_i (R_{NN_i})^{-1} \quad (23)$$

$$S_N = \sum_i (R_{MM_i})^{-1} \quad (24)$$

where  $N'$  represents the charge on the central nitrogen atom of the azide ion, the summations being performed exhaustively.

Data is available for the polarisability,  $\alpha$ , of the  $N_3^-$  ion and the value  $4.44 \text{ \AA}^3$ , the average of the anisotropic values quoted by Frech and Decius[14] was assumed. This value is close to  $\alpha_{Br} = 4.81 \text{ \AA}^3$  which was used for the azide ion in the previous calculations[1].

The characteristic energy of the  $N_3^-$  ion is estimated as 10% of the second ionisation potential of the  $N_3^-$  ion as calculated by Archibald and Sabin[15], which gives the value  $\epsilon = 13.1 \times 10^{-12} \text{ erg molecule}^{-1}$ . This is close to the value of  $\epsilon$  for the  $Br^-$  ion as used in our previous study  $4.0 \times 10^{-12} \text{ erg molecule}^{-1}$ .

The "electron numbers",  $p_i$ , were taken as 8 for all ions except  $Cl^-$ , where a value of 11 was used[16]. The values of  $U_{el}$ ,  $U_{el}$  and the total  $U_D$  are given in Table 1.

Previously, the repulsion energy,  $U_R$ , of the salts was calculated by assuming that the azide ion could be represented by an ellipsoid of revolution about the major axis.  $U_R$  was calculated using the Huggins and Mayer[17-19] approach. The ellipsoid axes used had lengths 1.764 and 2.545  $\text{\AA}$ . This model has been employed with the lower crystal data and the results are given in Table 1.

$U_R$ , as calculated by the new equation, in the form of the final term of eqn (7) is given in Table 1 and the coefficients of  $M_{ELBC}$  in eqn (6) are listed in Table 2 so that the value of the  $K(\partial M_{ELBC}/\partial a)_a$  term can be studied in the discussion section of this paper. The coefficients  $J_i$  give the quadratic dependence of the repulsion energy term, calculated taking  $\rho = 0.345 \text{ \AA}$  and  $a$  as the shortest metal-azide distance. The coefficients  $C_i$  for  $U_{ELBC}$  are generated from the expansion coefficients  $\alpha_i$  and  $\beta_i$  from eqn (6) are given in Table 2 for comparison with those in Table 1.

The coefficients,  $K_i$  ( $i = 0, 1, 2$ ) of the total lattice energy are calculated using the equation:

$$U_{TOT}(MN_3) = [C_0 - J_0 + U_D] + \sum_i (C_i - J_i)q_N^i = \sum_i K_i q_N^i \quad (25)$$

are given in Table 1.

### 3. RESULTS

Figure 1 displays a plot of  $\Delta H_f^\circ(N_3^-)(g)$  vs  $q_N$  from which an average intersection corresponding to:

$$\Delta H_f^\circ(N_3^-)(g) = 144 \text{ kJ mol}^{-1} \quad (26)$$

$$q_N = -0.91. \quad (27)$$

The figure also shows plots of  $\Delta H_f^\circ(N_3^-)(g)$  vs  $q_N$  using data for  $\Delta H_f^\circ(M^+)(g)$  from Halliwell and Nyburg's

Table 2. Evaluation of  $K(\partial M_{ELBC}/\partial a)_a$  term of eqn (9)

	NaN <sub>3</sub>	KN <sub>3</sub>	RbN <sub>3</sub>	CsN <sub>3</sub>	TlN <sub>3</sub>	
$\alpha_0$	2.487017	2.969977	2.969351	2.962249	2.969801	
$\alpha_2$	-31.4997	-8.196002	-6.922717	-5.227965	-7.195057	
$\alpha_4$	94.4078	151.304	144.117	134.623	145.649	
$\alpha_6$	60.5079	-145.124	-136.399	-125.954	-138.193	
$\alpha_8$	-12.2876	-251.396	-232.677	-198.345	-237.237	
$\alpha_{10}$	-1271.32	1220.69	1264.07	1273.14	1257.59	
$\alpha_{12}$	507.29	3384.05	2628.39	1787.04	2780.52	
$M_{ELBC}$	5393.93	-16277.9	-14026.5	-11372.8	-14486.4	
$\alpha_{14}$	8939.74	15075.7	14506.6	14398.7	14576.4	
$\alpha_{16}$	-234.993	88.3952	96.5017	106.308	94.8208	
$\beta_4$	2115.66	850.692	762.411	656.496	780.652	
$\beta_6$	-16424.0	-3891.54	-3442.03	-2940.76	-3532.41	
$\beta_{10}$	141107	14401.9	6831.40	4113.86	7372.04	
$\beta_{12}$	-1154911	-52366.8	-39882.7	-17806.2	-44293.9	
$\beta_{14}$	9802016	512636	375077	245667	401155	
$\beta_{16}$	-83771513	-2401698	-1680208	-1079255	-1811136	
$d(\text{\AA})$	1.1407	1.1800	1.1690	1.1656	1.1589	$N'-N$ distance
$a_d(\text{\AA})$	5.4880	6.1129	6.3098	6.5412	6.2080	cell parameter
$C_0$	629.6	675.0	653.8	629.2	664.6	
$C_1$	-298.7	-23.5	-16.2	-7.3	-17.9	
$C_2$	-78.4	36.4	30.8	26.6	32.1	
$G_1$	-503.7	-41.3	-37.2	-39.4	-37.8	
$G_2$	-264.3	-160.1	-133.0	-112.9	-138.8	
$U_{ELBC}$ (kJ mol <sup>-1</sup> )						
$K(\partial M_{ELBC}/\partial a)_a$						

paper[20], we obtain an average value for:

$$\Delta H_f^\circ(N_3^-)(g) = -315 \text{ kJ mol}^{-1} \quad (28)$$

$$q_N = -0.92 \quad (29)$$

and using data for  $\Delta H_f^\circ(M^+)(g)$  from the studies of Morris[21,22] an average value for:

$$\Delta H_f^\circ(N_3^-)(g) = -295 \text{ kJ mol}^{-1} \quad (30)$$

$$q_N = -0.86 \quad (31)$$

is obtained.

### 4. DISCUSSION

We discuss the results under six headings, calculating the lattice energies of thirteen salts from the thermodynamic data derived above.

#### (a) Applicability of the new equation to the azides

In essence the difference between the term by term approach used previously[1] and that used in this study is that  $U_R$ , the repulsion energy, was previously computed from the equation[17]:

$$U_R = bc \sum_i \exp[-(R_i - r_i^+ - r_i^-)/\rho] \quad (32)$$

where  $r_i^+$  and  $r_i^-$  are the Huggins "basic" radii of the anion and cation, employing an ellipsoidal model for the  $N_3^-$  ion. The present study uses the equation:

$$U_R = p_a \left[ U_{ELBC} + 6U_{el} + 8U_{el} - K \left( \frac{\partial M_{ELBC}}{\partial a} \right)_{a=a_m} \right] \quad (33)$$

As was noted in our study of the bifluorides[5], the

ellipsoid model of a linear ion (see Table 1, line 25) tends to exaggerate the charge density on the central atom (a charge distribution corresponding to  $q_N = -0.9$  indicates there is hardly any electronic charge on the central atom of the ion!) It is not surprising, therefore, that the repulsion energy in our present study (see Table 1, line 35) is higher than that calculated using the same ellipsoid model as before with the new crystal data (see Table 1, line 24).

The eqn (33) was essentially derived for cubic lattices with a single minimisation parameter,  $a$ ; in the cases of rhombohedral or tetragonal symmetry minimisation can be performed with respect to  $a$  and  $a$  in the former case and with respect to  $a$  and  $c$  in the latter. We have used the equation based on  $a$ , assuming the other lattice parameter to be constant in addition to the internal ion distance  $d$ . Minimisation with respect to the other lattice parameter should give analogous results for  $U_R$ .

We cannot leave the discussion of the new equation without comment about the excellent intersections given in the formation data graph.

#### (b) Enthalpy of formation of gaseous azide ion

The value for the enthalpy of formation of the gaseous azide ion is quoted as  $180 \text{ kJ mol}^{-1}$  in Technical note 270-3[3] and also in the CATCH tables[2] (with a quoted error of  $4 \text{ kJ mol}^{-1}$ ). The calculations performed using the new equation under test here, those performed using the term by term approach[1] made five years ago and those made fifteen years ago[4] all agree a value in the region of  $144 \text{ kJ mol}^{-1}$ . We therefore suggest that the value accepted in these tables is incorrect. The very localised region of the interactions encourages us in the belief that the calculations are reliable and moreover the previous (questionable) use of an ellipsoid model for the

ion appears *not* to be the factor responsible for the disparity apparent in the  $\Delta H_f^\circ(\text{N}_3^-)$  values.

(c) *Enthalpy of hydration of the gaseous azide ion*

N.B.S. Technical Note 270-3[3] gives a value for  $\Delta H_f^\circ(\text{N}_3^-)(\text{g}) = 180.7 \text{ kJ mol}^{-1}$  and  $\Delta H_f^\circ(\text{N}_3^-)(\text{aq}) = 275.1 \text{ kJ mol}^{-1}$ . Considering the process:  $\text{H}^+(\text{g}) + \text{N}_3(\text{g}) \xrightarrow{\Delta H} \text{H}^+(\text{aq}) + \text{N}_3(\text{aq})$ , we have:

$$\begin{aligned} \Delta H &= \Delta H_f^\circ(\text{H}^+(\text{aq})) + \Delta H_f^\circ(\text{N}_3(\text{aq})) - \Delta H_f^\circ(\text{H}^+(\text{g})) \\ &\quad - \Delta H_f^\circ(\text{N}_3(\text{g})) \\ &= \Delta H_{\text{hyd}}^\circ(\text{H}^+)(\text{g}) + \Delta H_{\text{hyd}}^\circ(\text{N}_3)(\text{g}) \end{aligned} \quad (35)$$

and hence:

$$\begin{aligned} \Delta H_{\text{hyd}}^\circ(\text{N}_3^-)(\text{g}) &= \Delta H_f^\circ(\text{H}^+(\text{aq})) + \Delta H_f^\circ(\text{N}_3(\text{aq})) \\ &\quad - \Delta H_f^\circ(\text{H}^+(\text{g})) - \Delta H_f^\circ(\text{N}_3(\text{g})) \\ &\quad - \Delta H_{\text{hyd}}^\circ(\text{H}^+)(\text{g}) \end{aligned} \quad (36)$$

taking  $\Delta H_f^\circ(\text{H}^+(\text{aq})) = 0 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{H}^+(\text{g})) = 1536.0 \text{ kJ mol}^{-1}$  and  $\Delta H_{\text{hyd}}^\circ(\text{H}^+)(\text{g}) = -1090.8 \pm 10.5 \text{ kJ mol}^{-1}$  from Ref. [23], we obtain:

$$\Delta H_{\text{hyd}}^\circ(\text{N}_3^-)(\text{g}) = -350.8 \pm 10.5 \text{ kJ mol}^{-1}. \quad (37)$$

Halliwell and Nyburg[20] gave a value for the conventional hydration enthalpy of the azide ion as  $-1389 \pm 12 \text{ kJ mol}^{-1}$ , from which we calculate the absolute value to be:

$$\Delta H_{\text{hyd}}^\circ(\text{N}_3^-)(\text{g}) = -298.2 \pm 12 \text{ kJ mol}^{-1}. \quad (38)$$

Gray and Waddington[4] assigned:

$$\Delta H_{\text{hyd}}^\circ(\text{N}_3^-)(\text{g}) = -330 \text{ kJ mol}^{-1} \quad (39)$$

on the basis of lyotropic numbers and using an average azide ion radius of  $2.042 \text{ \AA}$ .

The values derived in this study are  $-315 \text{ kJ mol}^{-1}$  on the basis of Halliwell and Nyburg's[20] data for  $\Delta H_{\text{hyd}}^\circ(\text{M}^+)(\text{g})$  and  $-295 \text{ kJ mol}^{-1}$  on the basis of Morris's[21, 22] values. Again the Technical Note assignment is at variance with our results.

The intersection for  $\text{CsN}_3$  in the plot using the Morris data is widely different from the intersections for  $\text{KN}_3$  and  $\text{RbN}_3$  with the  $\text{NaN}_3$  curve suggesting that the data for  $\Delta H_{\text{hyd}}^\circ(\text{Cs}^+)(\text{g})$  may be more accurate than that of Morris, or indeed that the Morris  $\text{Cs}^+$  value is inconsistent with the other  $\text{M}^+$  data he quotes. This point needs further investigation and for this reason we do not choose to select the most appropriate value for  $\Delta H_{\text{hyd}}^\circ(\text{N}_3)(\text{g})$  at this stage.

(d) *Charge distribution in  $\text{N}_3^-$  ion*

$q_N$  has been determined in many studies and has been assigned the following values chronologically:  $-0.83$  (valence electron calculation)[24],  $-0.60$  (molecular orbital calculation)[25],  $-0.857$  (NMR experimental value

for  $\text{NaN}_3$ )[26],  $-0.548$  (CNDO calculation)[27],  $-0.51$  (LCAOMOSCF calculation)[15],  $-0.52$  (lattice energy calculation)[1],  $-0.952$ ,  $-0.87$  (Quadrupole moment calculations)[28]  $-0.52$ ,  $-0.57$  (Population analysis)[28]. It is noticeable that while theoretical calculations tend to favour a charge of between  $-0.5$  and  $-0.6$  for  $q_N$ , experimental determinations put the value between  $-0.8$  and  $-0.9$ . The present study gave a value (averaged) of  $-0.9$  and in that it agrees with the latter range seems satisfactory.

(e) *Lattice energies of the metal azides*

On the basis of our assigned charge distribution,  $q_N = -0.90$  (average of eqns 27, 29 and 31) we find the total lattice potential energies of the univalent azides considered in this study to be:

$$U_{\text{pot}}(\text{NaN}_3) = 732 \text{ kJ mol}^{-1} \quad (40)$$

$$U_{\text{pot}}(\text{KN}_3) = 659 \text{ kJ mol}^{-1} \quad (41)$$

$$U_{\text{pot}}(\text{RbN}_3) = 637 \text{ kJ mol}^{-1} \quad (42)$$

$$U_{\text{pot}}(\text{CsN}_3) = 612 \text{ kJ mol}^{-1} \quad (43)$$

$$U_{\text{pot}}(\text{TlN}_3) = 689 \text{ kJ mol}^{-1}. \quad (44)$$

Based on the Born Haber cycle, the equations below, combined with our value for the enthalpy of formation of the gaseous azide ion enable us to calculate the lattice energies of all azides whose enthalpies of formation are known.

$$\begin{aligned} U_{\text{pot}}(\text{MN}_3) &= \Delta H_f^\circ(\text{H}^+)(\text{g}) + \Delta H_f^\circ(\text{N}_3)(\text{g}) \\ &\quad - \Delta H_f^\circ(\text{MN}_3)(\text{c}) \end{aligned} \quad (45)$$

and

$$\begin{aligned} U_{\text{pot}}(\text{M}(\text{N}_3)_2) &= \Delta H_f^\circ(\text{M}^{2+})(\text{g}) + 2\Delta H_f^\circ(\text{N}_3)(\text{g}) \\ &\quad - \Delta H_f^\circ(\text{M}(\text{N}_3)_2)(\text{c}) - \frac{5}{2}RT \end{aligned} \quad (46)$$

Use of these equations gives us the values:

$$U_{\text{pot}}(\text{AgN}_3) = 854 \text{ kJ mol}^{-1} \quad (47)$$

$$U_{\text{pot}}(\text{Pb}(\text{N}_3)_2) = 2170 \text{ kJ mol}^{-1} \quad (48)$$

$$U_{\text{pot}}(\text{Pb}(\text{N}_3)_2) = 2172 \text{ kJ mol}^{-1} \quad (49)$$

$$U_{\text{pot}}(\text{Zn}(\text{N}_3)_2) = 2840 \text{ kJ mol}^{-1} \quad (50)$$

$$U_{\text{pot}}(\text{Cd}(\text{N}_3)_2) = 2446 \text{ kJ mol}^{-1} \quad (51)$$

$$U_{\text{pot}}(\text{Cu}(\text{N}_3)_2) = 2730 \text{ kJ mol}^{-1} \quad (52)$$

$$U_{\text{pot}}(\text{Mn}(\text{N}_3)_2) = 2408 \text{ kJ mol}^{-1} \quad (53)$$

$$U_{\text{pot}}(\text{Sr}(\text{N}_3)_2) = 2056 \text{ kJ mol}^{-1} \quad (54)$$

$$U_{\text{pot}}(\text{Ca}(\text{N}_3)_2) = 2186 \text{ kJ mol}^{-1} \quad (55)$$

$$U_{\text{pot}}(\text{LiN}_3) = 812 \text{ kJ mol}^{-1}. \quad (56)$$

The only work, apart from ours, that we can compare results to is that of Gora[29] whose lattice energy values

$\text{NaN}_3$ )[26],  $-0.548$  (CNDO calculation)[27],  $-0.51$  (MOSCF calculation)[15],  $-0.52$  (lattice energy calculation)[1],  $-0.952$ ,  $-0.87$  (Quadrupole moment calculations)[28]  $-0.52$ ,  $-0.57$  (Population analysis)[28]. Noticeable that while theoretical calculations tend to give a charge of between  $-0.5$  and  $-0.6$  for  $q_N$ , experimental determinations put the value between  $-0.8$  and  $-0.9$ . The present study gave a value (averaged) of  $-0.85$  and in that it agrees with the latter range seems satisfactory.

#### Lattice energies of the metal azides

On the basis of our assigned charge distribution,  $-0.90$  (average of eqns 27, 29 and 31) we find the lattice potential energies of the univalent azides determined in this study to be:

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On the Born Haber cycle, the equations below, combined with our value for the enthalpy of formation of the azide ion enable us to calculate the lattice energies of all azides whose enthalpies of formation are

$$U_{\text{pot}}(\text{MN}_3) = \Delta H_f^\circ(\text{H}^+)(\text{g}) + \Delta H_f^\circ(\text{N}_3)(\text{g}) - \Delta H_f^\circ(\text{MN}_3)(\text{c}) \quad (45)$$

$$U_{\text{pot}}(\text{M}(\text{N}_3)_2) = \Delta H_f^\circ(\text{M}^{2+})(\text{g}) + 2\Delta H_f^\circ(\text{N}_3)(\text{g}) - \Delta H_f^\circ(\text{M}(\text{N}_3)_2)(\text{c}) - \frac{5}{2}RT \quad (46)$$

Use of these equations gives us the values:

$$U_{\text{pot}}(\text{AgN}_3) = 854 \text{ kJ mol}^{-1} \quad (47)$$

$$U_{\text{pot}}(\text{Pb}(\text{N}_3)_2)_{\text{monoclinic}} = 2170 \text{ kJ mol}^{-1} \quad (48)$$

$$U_{\text{pot}}(\text{Pb}(\text{N}_3)_2)_{\text{orthorhombic}} = 2172 \text{ kJ mol}^{-1} \quad (49)$$

$$U_{\text{pot}}(\text{Zn}(\text{N}_3)_2) = 2840 \text{ kJ mol}^{-1} \quad (50)$$

$$U_{\text{pot}}(\text{Cd}(\text{N}_3)_2) = 2446 \text{ kJ mol}^{-1} \quad (51)$$

$$U_{\text{pot}}(\text{Cu}(\text{N}_3)_2) = 2730 \text{ kJ mol}^{-1} \quad (52)$$

$$U_{\text{pot}}(\text{Mn}(\text{N}_3)_2) = 2408 \text{ kJ mol}^{-1} \quad (53)$$

$$U_{\text{pot}}(\text{Sr}(\text{N}_3)_2) = 2056 \text{ kJ mol}^{-1} \quad (54)$$

$$U_{\text{pot}}(\text{Ca}(\text{N}_3)_2) = 2186 \text{ kJ mol}^{-1} \quad (55)$$

$$U_{\text{pot}}(\text{LiN}_3) = 812 \text{ kJ mol}^{-1} \quad (56)$$

Only work, apart from ours, that we can compare ours to is that of Gora[29] whose lattice energy values

were essentially  $U_M$  values. The order of magnitude of the results for  $\text{Pb}(\text{N}_3)_2$  are similar to ours.

#### (f) Electron affinity of azide radical

Using the value of Evans, Yoffe and Gray[30] for the electron affinity of the azide radical,  $293 \pm 13 \text{ kJ mol}^{-1}$  we obtain a value

$$\Delta H_f^\circ(\text{N}_3)(\text{g}) = 443 \pm 13 \text{ kJ mol}^{-1} \quad (57)$$

#### REFERENCES

- Dixon H. P., Jenkins H. D. B. and Waddington T. C., *Chem. Phys. Letters* **10**, 600 (1971).
- Pedley J. B., CATCH Thermochemical Specimen Tables for Nitrogen, University of Sussex (1972).
- Parker V. B. et al., Tech. Note 270-3, Natl. Bur. Stds., Washington D.C. (1971).
- Gray P. and Waddington T. C., *Proc. Roy. Soc. A* **235**, 481 (1956).
- Dixon H. P., Jenkins H. D. B. and Waddington T. C., *J. Chem. Phys.* **57**, 4388 (1972).
- Müller Von U., *Z. Anorg. Allg. Chem.* **392**, 159 (1972).
- Jenkins H. D. B. and Waddington T. C., *Chem. Phys. Letters* **31**, 369 (1975).
- Jenkins H. D. B., *J. Chem. Soc. Faraday II* **72**, 1569 (1976).
- Gray P. and Waddington T. C., *Proc. Roy. Soc. A* **235**, 106 (1956).
- Born M. and Mayer J. E., *Z. Physik* **75**, 1 (1932).
- Bertaut E. F., *J. Phys. Radium* **13**, 499 (1952).
- Jenkins H. D. B., *Chem. Phys. Letters* **9**, 473 (1971).
- Jenkins H. D. B., *Chem. Phys. Letters* **20**, 155 (1973).
- Frech K. and Decius J. C., *J. Chem. Phys.* **51**, 5315 (1969).
- Archibald T. W. and Sabin J. R., *J. Chem. Phys.* **55**, 1821 (1971).
- Alcock N. W. and Jenkins H. D. B., *J. Chem. Soc. Dalton Trans.* 1907 (1974).
- Huggins M. L., *J. Chem. Phys.* **5**, 143 (1937).
- Mayer J. E., *J. Chem. Phys.* **1**, 327 (1933).
- Huggins M. L. and Mayer J. E., *J. Chem. Phys.* **1**, 643 (1933).
- Hallwell H. F. and Nyburg S. C., *Trans. Faraday Soc.* **59**, 1126 (1963).
- Morris D. F. C., *Structure and Bonding* **4**, 63 (1968).
- Morris D. F. C., *Structure and Bonding* **6**, 157 (1969).
- Lister M. W., Nyburg S. C. and Poyntz R. B., *J. Chem. Soc. Faraday I* **70**, 685 (1974).
- Bonneway A. and Daudel R., *Comp. Rend. Acad. Sci. (Paris)* **230**, 2300 (1950).
- Müller V. H., *Z. Naturforsch.* **19B**, 867 (1964).
- Campbell I. D. and Coogan C. K., *J. Chem. Phys.* **44**, 2075 (1966).
- Hollander J. M., Hendrickson D. N. and Jolly W. T., *J. Chem. Phys.* **49**, 3315 (1968).
- Gora T. and Kemmeyer P. J., *J. Chem. Phys.* **57**, 3579 (1972).
- Gora T., *J. Phys. Chem. Solids* **32**, 529 (1971).
- Evans B. L., Yoffe A. D. and Gray P., *Chem. Rev.* **59**, 515 (1959).
- Rossini F. D. et al., N.B.S. Circular 500, Natl. Bur. Stds., Washington D.C. (1952).
- Dassett W. E., *Inorganic Energetics*, Penguin Science Books, London (1970).
- Hendricks S. B. and Pauling L., *J. Am. Chem. Soc.* **47**, 2904 (1925).

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ION MODEL INDEPENDENT STUDIES OF HYDROGEN BONDING  
AND THE THERMOCHEMISTRY OF BIFLUORINE SALTS

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# Ion Model Independent Studies of Hydrogen Bonding and the Thermochemistry of Bifluoride Salts

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Quantum mechanical based studies of the enthalpy change,  $\Delta H_f^\ominus$ , for the process (measuring the hydrogen bond strength in the bifluoride ion):



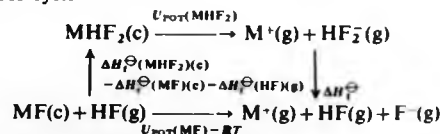
are at variance with studies based on classical lattice energy calculations. One of the difficulties in the latter calculations has been that of making reliable calculations of the repulsion energy  $U_R$  between the non-spherical  $\text{HF}_2^-$  ions, requiring the choice of a suitable model to represent the ion. The recently proposed equation:

$$U_R = \rho/a[U_{\text{ELEC}} + 6U_{\text{dd}} + 8U_{\text{qd}} - K(2ME_{\text{ELEC}}/\epsilon a)a, a = a_0]$$

is used for ion model independent calculations of  $U_R$ . Incorporation of the results to calculate the lattice energy of alkali metal bifluoride salts and  $\Delta H_f^\ominus(\text{HF}_2)(\text{g})$  leads to values for  $\Delta H_f^\ominus$  which accord with the numerous quantum mechanical estimates. The results of the studies in this paper give, for the lattice potential energies of the bifluorides:  $U_{\text{POT}}(\text{LiHF}_2) = 893 \pm 20 \text{ kJ mol}^{-1}$ ,  $U_{\text{POT}}(\text{NaHF}_2) = 788 \pm 14 \text{ kJ mol}^{-1}$ ,  $U_{\text{POT}}(\text{KHF}_2) = 703 \text{ kJ mol}^{-1}$ ,  $U_{\text{POT}}(\text{RbHF}_2) = 674 \pm 5 \text{ kJ mol}^{-1}$  and  $U_{\text{POT}}(\text{CsHF}_2) = 646 \pm 4 \text{ kJ mol}^{-1}$ , for  $\Delta H_f^\ominus(\text{HF}_2)(\text{g})$  a value of  $-728 \pm 9 \text{ kJ mol}^{-1}$  and for  $\Delta H_f^\ominus$  a value  $= 176 \pm 6 \text{ kJ mol}^{-1}$ . We estimate  $U_{\text{POT}}(\text{NH}_4\text{HF}_2) = 705 \pm 9 \text{ kJ mol}^{-1}$ .

## INTRODUCTION

If the lattice energy of an alkali metal bifluoride salt,  $U_{\text{POT}}(\text{MHF}_2)$  is known, the Born-Fajans-Haber cycle<sup>1</sup>



can be used to calculate the enthalpy of the process:



provided the lattice potential energy,  $U_{\text{POT}}(\text{MF})$  of the corresponding alkali metal fluoride, MF, is known.

$$\Delta H_f^\ominus = U_{\text{POT}}(\text{MF}) - U_{\text{POT}}(\text{MHF}_2) - RT - \Delta H_f^\ominus(\text{MHF}_2)(\text{c}) + \Delta H_f^\ominus(\text{MF})(\text{c}) + \Delta H_f^\ominus(\text{HF})(\text{g}). \quad (1)$$

In attempting to calculate the repulsion component of the lattice energy of a salt involving an ion like the bifluoride  $\text{HF}_2^-$  ion, one is normally forced to adopt a



"model" for the non-spherical  $\text{HF}_2^-$  ion (fig. 1). Models involving explicit consideration of only the terminal fluorine atoms have been considered,<sup>2-4</sup> as have models in which the bifluoride ion is represented by the simplest solid figure which reproduces the full axial symmetry of the ion.<sup>2-4</sup> However, the former model doubtless neglects the distorting effect of the central hydrogen (and thus presumably offers an upper limit for the magnitude of the repulsion energy  $U_R$ ) while the latter model, when employed within the framework of the Huggins and Mayer<sup>5,6</sup> approach to the calculation of  $U_R$ , as expressed by the equation:

$$U_R = bc \sum_{\text{ions}} \exp [-(R_i - \bar{r}_+ - \bar{r}_-)/\rho] \quad (2)$$

(where  $\bar{r}_+$ ,  $\bar{r}_-$  are the Huggins "basic" radii of the anion and cation and  $R_i$  is the distance between their centres of gravity) leads to uncertainties due to the necessity of choosing appropriate ellipsoid radii. The model itself tends to overemphasise the contribution made to the electron density in the region of the hydrogen atom. Notwithstanding these considerations Waddington<sup>2</sup> has obtained  $\Delta H_f^\ominus = 244 \text{ kJ mol}^{-1}$ , Neckel, Kuzmany and Vinek<sup>7</sup> have found  $\Delta H_f^\ominus = 234 \text{ kJ mol}^{-1}$  and Dixon, Jenkins and Waddington<sup>3,4</sup> have obtained  $\Delta H_f^\ominus = 252 \text{ kJ mol}^{-1}$  by means of lattice energy calculations for  $\text{MHF}_2$  coupled with the use of eqn (1). These values of  $\Delta H_f^\ominus$  spanning the range 230–255  $\text{kJ mol}^{-1}$  are higher in the main than the values obtained by the quantum mechanical studies based on the *ab initio* calculations of Bessis and Bratoz<sup>8</sup> ( $\Delta H_f^\ominus = 191 \text{ kJ mol}^{-1}$ ); McLean and Yoshimine<sup>9</sup> ( $\Delta H_f^\ominus = 188 \text{ kJ mol}^{-1}$ ); Kollman and Allen<sup>10</sup> ( $\Delta H_f^\ominus = 218 \text{ kJ mol}^{-1}$ ); Noble and Kurtzborn<sup>11</sup> ( $\Delta H_f^\ominus = 167 \text{ kJ mol}^{-1}$ ); Almlöf<sup>12</sup> ( $\Delta H_f^\ominus = 213 \text{ kJ mol}^{-1}$ ); Spencer, Casey, Buckfelder and Schreiber<sup>13</sup> ( $\Delta H_f^\ominus = 136 \text{ kJ mol}^{-1}$ ); Stoegard, Strich, Almlöf and Roos<sup>14</sup> [ $\Delta H_f^\ominus = 222 \text{ kJ mol}^{-1}$  (SCF) and  $234 \text{ kJ mol}^{-1}$  (CI)]. A recent discussion of these values is to be found in ref. (15).

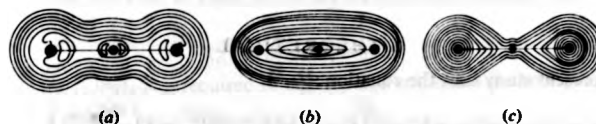
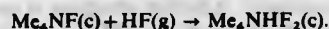


FIG. 1.—Potential energy surfaces (a) for true  $\text{HF}_2^-$  ion; (b) for ellipsoid model of  $\text{HF}_2^-$  ion and (c) for separated  $\text{F}^-$  ion model for ion.

The very early results obtained from the electrostatic model of Fyfe<sup>16</sup> ( $\Delta H_f^\ominus = 241 \text{ kJ mol}^{-1}$ ), from the model of Davies<sup>17</sup> based on ion-dipole interactions ( $\Delta H_f^\ominus = 200 \text{ kJ mol}^{-1}$ ) are based on simplified models, and the CNDO/2 calculation of Murphy, Bhat and Rao<sup>18</sup> which gives  $\Delta H_f^\ominus = 1255 \text{ kJ mol}^{-1}$  is so much in disagreement with other quantum mechanical approaches that this value can be disregarded, their value based on extended Hückel calculations ( $\Delta H_f^\ominus = 163 \text{ kJ mol}^{-1}$ ) is probably more reliable. The CNDO studies of Schuster<sup>19</sup> also indicate the CNDO approach to be unreliable ( $\Delta H_f^\ominus = 444 \text{ kJ mol}^{-1}$ ) for the estimation of enthalpy data of this type. The quantum mechanical results extend over a range 130–234  $\text{kJ mol}^{-1}$  which is lower than  $\Delta H_f^\ominus$  derived from thermochemical approaches.

The commonly regarded "experimental" value for  $\Delta H_f^\ominus$  is close to 155  $\text{kJ mol}^{-1}$ , derived by Harrel and McDaniel<sup>20</sup> from measurements of the enthalpy change of the reaction:



## Enthalpies of Hydrogen Bonding of Bifluoride Salts

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Received, 1976

Enthalpy change,  $\Delta H_f^\ominus$ , for the process (measuring

+ F (g)

energy calculations. One of the difficulties in the calculation of the repulsion energy  $U_R$  in the case of a suitable model to represent the ion.

$K(\epsilon_{\text{MELEC}}/\epsilon_0 a)$ ,  $a = a_0$

1. Incorporation of the results to calculate  $\Delta H_f^\ominus(\text{HF}_2(\text{g}))$  leads to values for  $\Delta H_f^\ominus$  which are in good agreement with the values obtained from the studies in this series:  $U_{\text{TOT}}(\text{LiHF}_2) = 893 \pm 20 \text{ kJ mol}^{-1}$ ,  $U_{\text{TOT}}(\text{RbHF}_2) = 674 \pm 5 \text{ kJ mol}^{-1}$ ,  $U_{\text{TOT}}(\text{NH}_4\text{HF}_2) = 705 \pm 9 \text{ kJ mol}^{-1}$  and  $U_{\text{TOT}}(\text{NH}_4\text{HF}_2) = 705 \pm 9 \text{ kJ mol}^{-1}$ .

## INTRODUCTION

In the case of the bifluoride salt,  $U_{\text{TOT}}(\text{MHF}_2)$  is known, the

$\text{M}^+(\text{g}) + \text{HF}_2^-(\text{g})$

$\text{M}^+(\text{g}) + \text{HF}(\text{g}) + \text{F}^-(\text{g})$

$\text{M}^+(\text{g}) + \text{HF}(\text{g}) + \text{F}^-(\text{g})$

process:

$\text{M}^+(\text{g}) + \text{F}^-(\text{g})$

of the corresponding alkali metal

$\Delta H_f^\ominus(\text{MHF}_2(\text{c})) +$

$\Delta H_f^\ominus(\text{MF}(\text{c})) + \Delta H_f^\ominus(\text{HF}(\text{g})). \quad (1)$

component of the lattice energy of a salt, one is normally forced to adopt a

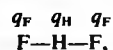
They assume that the lattice energies  $U_{\text{POT}}(\text{Me}_4\text{NF})$  and  $U_{\text{POT}}(\text{Me}_4\text{NHF}_2)$  will be within 10 kJ or so of each other and hence their measurement reflects  $\Delta H_1$ . This assumption seems to be invalid when applied to the results obtained, using the simple Born-Mayer approach, from studies on  $U_{\text{POT}}(\text{Me}_4\text{NCl}) = 506 \text{ kJ mol}^{-1}$  and  $U_{\text{POT}}(\text{Me}_4\text{NHCl}_2) = 476 \text{ kJ mol}^{-1}$ ,<sup>21</sup> where

$$\Delta U = U_{\text{POT}}(\text{Me}_4\text{NCl}) - U_{\text{POT}}(\text{Me}_4\text{NHCl}_2) = 30 \text{ kJ mol}^{-1}.$$

If the same  $\Delta U$  is preserved for the fluorides, the revised Harrel and McDaniel value for  $\Delta H_1^\circ$  would be  $\sim 185 \text{ kJ mol}^{-1}$ .

A recently proposed equation<sup>22, 23</sup> offers a means of calculating the repulsion component,  $U_R$ , for the bifluorides using the subterfuge of avoiding the specification of a "model" for the non-spherical  $\text{HF}_2^-$  ion. In this paper we examine the use of this equation and compare the thermodynamic parameters derived for the  $\text{HF}_2^-$  ion with those previously<sup>3, 4</sup> obtained by more conventional methods, the essential difference in methodology being in the calculation of  $U_R$ .

Various distributed charges are assigned to the linear bifluoride ion,



and the lattice potential energy,  $U_{\text{POT}}(\text{MHF}_2)$ , is calculated as a function of  $q_F$  which is related to  $q_H$  by the expression:

$$q_H = -[1 + 2q_F]. \quad (3)$$

The equations take the standard form:

$$U_{\text{POT}}(\text{MHF}_2) = \sum_{i=0}^2 D_i q_F^i \quad (4)$$

where  $D_i$  are constants depending on the alkali metal M for each lattice considered

### THEORETICAL

The present study uses the equation:<sup>22, 23</sup>

$$U_{\text{POT}} = U_{\text{ELEC}} + U_{dd} + U_{qd} - \frac{\rho}{a} \left[ U_{\text{ELEC}} + 6U_{dd} + 8U_{qd} - K \left( \frac{\partial M_{\text{ELEC}}}{\partial a} \right)_{d,a=a_0} \right] \quad (5)$$

which is derived by direct minimisation having:

$$U_R = \frac{\rho}{a} \left[ U_{\text{ELEC}} + 6U_{dd} + 8U_{qd} - K \left( \frac{\partial M_{\text{ELEC}}}{\partial a} \right)_{d,a=a_0} \right]. \quad (6)$$

The equation was derived for cubic lattices with a single parameter  $a$ .  $U_{\text{ELEC}}$  is the electrostatic component of the lattice energy,  $U_{dd}$  and  $U_{qd}$  are the dipole-dipole and quadrupole-dipole terms making up the dispersion energy  $U_D$ ,  $M_{\text{ELEC}}$  is the electrostatic Madelung parameter,  $\rho$  is the repulsion exponent,  $a$  is the shortest anion-cation distance,  $d$  is the internal H—F distance in the case of a bifluoride ion and  $K$  is the conversion factor from units of  $\text{e}^2 \text{Å}^{-1}$  to  $\text{kJ mol}^{-1}$ . The equation has several advantages for non-spherical ions.  $\rho$  is a multiplicative parameter in eqn (5), rather than being exponentiated as in eqn (2) ( $U_R$  is, therefore, less sensitive to choice of  $\rho$ ). Eqn (5) requires no assignment of radii to the ions involved and, since it appears to be valid for the azides,<sup>24</sup> extension to the case of the symmetrically similar bifluorides should be immediate. A further advantage of our equation concerns the possibility of reduced errors, in that if  $U_{dd}$  and  $U_{qd}$  contain errors, then a similar

$U_{\text{POT}}(\text{Me}_4\text{NF})$  and  $U_{\text{POT}}(\text{Me}_4\text{NHF}_2)$  will be their measurement reflects  $\Delta H_1$ . This applied to the results obtained, using values on  $U_{\text{POT}}(\text{Me}_4\text{NCl}) = 506 \text{ kJ mol}^{-1}$  and

$$\text{Me}_4\text{NHCl}_2 = 30 \text{ kJ mol}^{-1}.$$

oxides, the revised Harrel and McDaniel

ers a means of calculating the repulsion e subterfuge of avoiding the specification ion. In this paper we examine the use ionic parameters derived for the  $\text{HF}_2^-$  ion ore conventional methods, the essential ulation of  $U_R$ .

l to the linear bifluoride ion,

$$\begin{matrix} q_F \\ -F, \end{matrix}$$

$z_2$ ), is calculated as a function of  $q_F$  which

$$-2q_F]. \quad (3)$$

$$= \sum_{i=0}^2 D_i q_F^i \quad (4)$$

alkali metal M for each lattice considered.

## METHODICAL

23

$$+6U_{dd} + 8U_{qd} - K \left( \frac{\partial M_{\text{ELEC}}}{\partial a} \right)_{d,a=a_0} \quad (5)$$

ving:

$$1 - K \left( \frac{\partial M_{\text{ELEC}}}{\partial a} \right)_{d,a=a_0} \quad (6)$$

tices with a single parameter  $a$ .  $U_{\text{ELEC}}$  is energy.  $U_{dd}$  and  $U_{qd}$  are the dipole-dipole the dispersion energy  $U_D$ ,  $M_{\text{ELEC}}$  is the he repulsion exponent,  $a$  is the shortest -F distance in the case of a bifluoride ion of  $e^2 \text{ Å}^{-1}$  to  $\text{kJ mol}^{-1}$ . The equation has  $\rho$  is a multiplicative parameter in eqn (5), (2) ( $U_R$  is, therefore, less sensitive to choice of radii to the ions involved and, since it ion to the case of the symmetrically similar er advantage of our equation concerns the  $U_{dd}$  and  $U_{qd}$  contain errors, then a similar

"scaled" error will occur in  $U_R$  as a consequence of eqn (6). When eqn (6) is then employed, within the context of eqn (5), the errors in  $U_R$ , in  $U_{dd}$  and  $U_{qd}$  will tend to counterbalance one another.

## CALCULATIONS

### (I) CRYSTAL STRUCTURE DATA

$\text{LiHF}_2$  and  $\text{NaHF}_2$  have rhombohedral symmetry. The unimolecular cells have, for  $\text{LiHF}_2$ ,  $a = 4.725 \text{ Å}$ ,  $\alpha = 37^\circ 3' 25''$  and for  $\text{NaHF}_2$ ,  $a = 5.006 \text{ Å}$ ,  $\alpha = 40^\circ 38' 26''$ .  $\text{KHF}_2$ ,  $\text{RbHF}_2$  and  $\text{CsHF}_2$  are tetragonal body centred lattices with tetramolecular cells of dimensions  $a = 5.67$ ,  $c = 6.81 \text{ Å}$ ;  $a = 5.90$ ,  $c = 7.26 \text{ Å}$  and  $a = 6.14$ ,  $c = 7.84 \text{ Å}$  respectively.<sup>27</sup>

### (II) REPULSION ENERGY CALCULATIONS

$U_R$  can be calculated in the form:

$$U_R = \frac{\rho}{a} \sum_{i=0}^2 R_i q_F^i = \sum_{i=0}^2 C_i q_F^i \quad (7)$$

where  $R_i$  and  $C_i$  are charge independent coefficients and  $q_F$  is the charge on the terminal fluorine atoms of the anion.

For the purposes of calculating  $R_i$ ,  $U_{\text{ELEC}}$  was taken to have the parametric form:

$$U_{\text{ELEC}} = \sum_{i=0}^2 A_i q_F^i \quad (8)$$

$U_{dd}$  and  $U_{qd}$  [the former equivalent to  $U_D$  in ref. (3)] were calculated as described below [sections (III) and (IV)].

We have

$$R_0 = A_0 + 6U_{dd} + 8U_{qd} \quad (9)$$

and:

$$R_i (i \neq 0) = A_i - B_i \quad (10)$$

where  $K (\partial M_{\text{ELEC}} / \partial a)_{d,a=a_0}$  required in eqn (6) was calculated in the form:

$$K \left( \frac{\partial M_{\text{ELEC}}}{\partial a} \right)_{d,a=a_0} = \sum_{i=1}^2 B_i q_F^i \quad (11)$$

The coefficients  $B_i$  have been calculated by expanding the Madelung parameter,  $M_{\text{ELEC}}$ , (based on the cell length  $a_0$  as the characteristic distance), and defined by:

$$M_{\text{ELEC}} = U_{\text{ELEC}} \cdot a_0 / K \quad (12)$$

as a series expansion:

$$M_{\text{ELEC}} = \alpha_0 + \left( \sum_{\substack{n=2 \\ \text{even}}}^8 \alpha_n \lambda^n \right) q_F + \left( \sum_{\substack{n=2 \\ \text{even}}}^{20} \beta_n \lambda^n \right) q_F^2 \quad (13)$$

where:

$$\lambda = \left( \frac{d}{a_0} \right) \quad (14)$$

and hence:

$$K \left( \frac{\partial M_{\text{ELEC}}}{\partial a} \right)_{d,a=a_0} = -\frac{K}{a_0} \left[ \left( \sum_{\substack{n=2 \\ \text{even}}}^8 n \alpha_n \lambda^{n-1} \right) q_F + \left( \sum_{\substack{n=2 \\ \text{even}}}^{20} n \beta_n \lambda^{n-1} \right) q_F^2 \right] = \sum_{i=1}^2 B_i q_F^i \quad (15)$$

(III) DIPOLE-DIPOLE DISPERSION TERM,  $U_{dd}$ 

To calculate the induced dipole-induced dipole term,  $U_{dd}$  we employ the equations:

$$U_{dd} = C_{+-} S_L^{+-} + \frac{1}{2}(C_{++} S_L^{++} + C_{--} S_L^{--}) \quad (16)$$

where

$$C_{ij} = \frac{3}{2} e^4 \frac{Q_{i00}^2 Q_{j00}^2}{\epsilon_i + \epsilon_j} \quad (17)$$

where the terms used above are defined below [Section (IV)].

(IV) QUADRUPOLE-DIPOLE DISPERSION TERM,  $U_{qd}$ 

This term was not calculated in our previous study.<sup>3</sup> To calculate the term we employ the equations:

$$U_{qd} = d_{+-} S_8^{+-} + \frac{1}{2}(d_{++} S_8^{++} + d_{--} S_8^{--}) \quad (18)$$

where

$$d_{ij} = \frac{3}{2} c_{ij} \left( \frac{Q_{i00}^2}{p_i} + \frac{Q_{j00}^2}{p_j} \right) \quad (19)$$

and

$$Q_{i00}^2 = \frac{3}{2} \alpha_i \epsilon_i / e^2 \quad (20)$$

and

$$S_n^{ij} = \sum_{\text{ions}} (R_{ij})^{-n} \quad (21)$$

$C_{ij}$  are the coefficients of the dipole-dipole dispersion energy term of the previous study,<sup>3</sup>  $\alpha_i$  are polarisability of the ions,  $\epsilon_i$  the characteristic energy of the ions,  $e$  the electronic charge and  $p_i$  the "electron numbers" (taken as 8) [see ref. (5)]. The summations  $S_8^{ij}$  and  $S_8^{ij}$  were performed and the resulting values for  $U_{dd}$  and for  $U_{qd}$  are cited in table 1.

(V)  $U_R$  FOR THE RHOMBOHEDRAL SALTS

The expansions of the form of eqn (13) were computed for lithium and sodium bifluoride using a program written by Herzig, Kuzmany and Neckel<sup>28</sup> as modified by Jenkins and Pratt.<sup>29</sup> The coefficients  $\alpha_n$  and  $\beta_n$  ( $n$  even) are given in the table 1 from which the coefficients  $B_n$  of eqn (15) have been calculated using the values of  $d$  and  $a_0$  listed therein.  $U_R$  is calculated assuming a value for  $\rho$  of 0.345 Å and  $a$ , the shortest cation-anion distance (M—F) is as quoted. The coefficients  $R_i$  and  $C_i$  of eqn (7) are then found. In the case of rhombohedral salts values of  $\beta_n$ ,  $n \leq 20$  were required for convergence.

(VI)  $U_R$  FOR TETRAGONAL SALTS

Neckel, Kuzmany and Vinek<sup>7</sup> have evaluated the coefficients  $\alpha_n$  ( $n = 0, 2, 4, 6$  and 8) and  $\beta_n$  ( $n = 2, 4, 6, 8, 10, 12, 14$  and 16) for the tetragonal alkali metal bifluorides. The coefficients  $B_i$ ,  $C_i$  and  $R_i$  deriving from their results are given in the table together with the parameters  $d$ ,  $a$  and  $a_0$  used.

E DISPERSION TERM,  $U_{dd}$ 

ced dipole term,  $U_{dd}$  we employ the equations:

$$\frac{1}{2}(C_{++}S_L^{++} + C_{--}S_L^{--}) \quad (16)$$

$$0 \quad (17)$$

l below [Section (IV)].

POLE DISPERSION TERM,  $U_{qd}$ 

r previous study.<sup>3</sup> To calculate the term we

$$\frac{1}{2}(d_{++}S_S^{++} + d_{--}S_S^{--}) \quad (18)$$

$$\frac{Q_{f00}^2}{p_j} \quad (19)$$

$$(20)$$

$$(21)$$

-dipole dispersion energy term of the previous  
,  $\epsilon_i$  the characteristic energy of the ions,  $\epsilon$  the  
n numbers" (taken as 8) [see ref. (5)]. The  
d and the resulting values for  $U_{dd}$  and for

## RHOMBOHEDRAL SALTS

i (13) were computed for lithium and sodium  
Herzig, Kuzmany and Neckel<sup>28</sup> as modified  
ts  $\alpha_n$  and  $\beta_n$  ( $n$  even) are given in the table I from  
ave been calculated using the values of  $d$  and  
suming a value for  $\rho$  of 0.345 Å and  $a$ , the  
) is as quoted. The coefficients  $R_i$  and  $C_i$  of  
rhombohedral salts values of  $\beta_n$ ,  $n \leq 20$  were

## TETRAGONAL SALTS

e evaluated the coefficients  $\alpha_n$  ( $n = 0, 2, 4, 6$   
, 14 and 16) for the tetragonal alkali metal  
nd  $R_i$  deriving from their results are given in  
 $d$ ,  $a$  and  $a_0$  used.

## (VII) LATTICE POTENTIAL ENERGIES

The total lattice potential energy for the salts is given by eqn (4)

where

$$D_0 = A_0 + U_{dd} + U_{qd} - C_0 \quad (22)$$

and

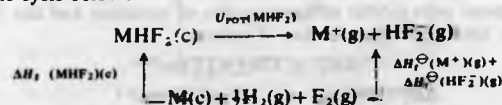
$$D_i (i \neq 0) = A_i - C_i \quad (23)$$

TABLE 1.—PARAMETERISATION OF EQN (4), (7), (8), (11), (13), (15), (16) AND (18) FOR ALKALI METAL BIFLUORIDES (ALL UNITS IN  $\text{kJ mol}^{-1}$ )

		rhombohedral salts		tetragonal salts			notes
		LiHF <sub>2</sub>	NaHF <sub>2</sub>	KHF <sub>2</sub>	RbHF <sub>2</sub>	CaHF <sub>2</sub>	
$U_{elec}$	$A_0$	707.6	708.2	727.3	697.9	667.6	eqn (8)
	$A_1$	-527.5	-303.8	-11.1	-5.7	2.2	
	$A_2$	-177.3	-91.1	47.4	39.7	33.6	
$U_D$	$U_{dd}$	22.8	24.6	35.5	40.1	46.7	eqn (16)
	$U_{qd}$	1.4	1.6	2.6	3.5	5.2	eqn (18)
	$U_D$	24.2	26.2	38.1	43.6	51.9	$U_D = U_{dd} + U_{qd}$
$M_{elec}$	$\alpha_0$	2.406 562	2.552 179	2.968 38	2.963 58	2.990 41	eqn (13)
	$\alpha_2$	-37.3207	-25.8416	-6.553 70	-5.456 12	-3.871 08	and (15)
	$\alpha_4$	103.498	85.5631	142.037	135.892	127.053	
	$\alpha_6$	63.2901	50.1252	-134.023	-127.297	-118.272	
	$\alpha_8$	-120.736	-109.304	-226.044	-203.514	-164.679	
	$\alpha_{10}$	0	0	0	0	0	
	$\beta_4$	-291.725	-185.083	98.7228	105.043	113.333	
	$\beta_6$	2818.36	1557.15	738.248	670.016	580.808	
	$\beta_8$	-24303.2	-10638.9	-3324.21	-3003.20	-2607.06	
	$\beta_{10}$	223.593	85.637.8	6148.63	4421.54	2599.87	
	$\beta_{12}$	-2.005 672	-632.951	-61.496.4	-49.842.2	-37.674.8	
	$\beta_{14}$	18.517 098	4.890 452	367.594	319.398	267.799	
	$\beta_{16}$	-171.999 407	-38.265 499	-10.592 400	-10.490 200	-10.392 400	
	$\beta_{18}$	1.612 021 290	298.554 719	—	—	—	
	$\beta_{20}$	-15.232 157 900	-2.356 997 330	—	—	—	
$K(eM_{elec}/ze) d, n = \infty$	$B_1$	836.4	475.5	-78.1	-68.0	-65.6	eqn (11)
	$B_2$	560.0	296.4	-204.4	-169.2	-141.5	
$U_{in}$	$R_0$	855.6	868.6	961.1	966.5	989.4	eqn (7)
	$R_1$	-1363.9	-779.1	67.0	62.3	67.8	
	$R_2$	-737.3	-387.5	251.8	208.9	175.1	
	$C_0$	105.5	107.3	100.2	96.4	93.8	
	$C_1$	-168.1	-96.2	7.0	6.2	6.4	
cell parameters	$d/\text{Å}$	1.135	1.134	1.13	1.13	1.13	
	$a_0/\text{Å}$	4.725	5.006	5.67	5.90	6.14	
	$a/\text{Å}$	2.799	2.794	3.31	3.46	3.64	
anion-cation dist.	$u/\text{Å}$	2.799	2.794	3.31	3.46	3.64	
$U_{TOT}$	$D_0$	626.3	627.1	665.2	645.1	625.6	eqn (4)
	$D_1$	-359.4	-207.6	-18.1	-11.9	-4.2	
	$D_2$	-86.4	-43.3	21.2	18.9	17.0	

(VIII) ENTHALPY OF FORMATION OF  $\text{HF}_2^-$  GASEOUS ION,  $\Delta H_f^\circ(\text{HF}_2^-)(g)$ 

Using the cycle below:



we have :

$$\Delta H_f^\ominus(\text{HF}_2^-)(g) = U_{\text{POT}}(\text{MHF}_2) + \Delta H_f^\ominus(\text{MHF}_2)(c) - \Delta H_f^\ominus(\text{M}^+)(g) = \sum_{i=0}^2 E_i q_F^i \quad (24)$$

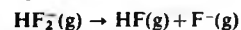
$$E_0 = D_0 + \Delta H_f^\ominus(\text{MHF}_2)(c) - \Delta H_f^\ominus(\text{M}^+)(g) \quad (25)$$

$$E_i (i \neq 0) = D_i \quad (26)$$

where the parameters  $E_i$  are cited in table 2.

#### (IX) HYDROGEN BOND STRENGTH $\Delta H_1^\ominus$

The enthalpy,  $\Delta H_1^\ominus$ , of the process :



represents a measure of the strength of the hydrogen bond in the bifluoride ion.

Parameterising eqn (1) in the form :

$$\Delta H_1^\ominus = \sum_{i=0}^2 F_i q_F^i \quad (27)$$

where

$$F_0 = U_{\text{POT}}(\text{MF}) - D_0 - RT - \Delta H_f^\ominus(\text{MHF}_2)(c) + \Delta H_f^\ominus(\text{HF})(g) + \Delta H_f^\ominus(\text{MF})(c) \quad (28)$$

$$F_i (i \neq 0) = -D_i \quad (29)$$

we obtain the coefficients listed in table 2.

The thermodynamic parameter,  $\Delta H_f^\ominus(\text{HF})(g) = -271.1 \text{ kJ mol}^{-1}$ , was taken from ref. (30). All other thermodynamic data employed are cited in the tables.

TABLE 2.—THERMODYNAMIC PARAMETERS (units in  $\text{kJ mol}^{-1}$ )

	LiHF <sub>2</sub>	NaHF <sub>2</sub>	KHF <sub>2</sub>	RbHF <sub>2</sub>	CsHF <sub>2</sub>	note
$\Delta H_f^\ominus(\text{MHF}_2)(c)$	-923.9	-906.2	-920.4	-909.2	-904.2	ref. (3)
$\Delta H_f^\ominus(\text{M}^+)(g)$	687.1	609.8	514.2	494.9	460.6	ref. (31)
$\Delta H_f^\ominus(\text{HF}_2^-)(g)$	$E_0$	-984.7	-888.9	-769.4	-759.0	-739.1
	$E_1$	-359.4	-207.6	-18.1	-11.9	-4.2
	$E_2$	-86.4	-43.3	21.2	18.9	17.0
$U_{\text{POT}}$	1030	905	800	765	734	ref. (32)
$\Delta H_f^\ominus(\text{MF})(c)$	-611.7	-569.0	-562.8	-551.5	-545.2	ref. (33)
$\Delta H_1^\ominus$	$F_0$	442.3	341.5	218.8	204.0	193.7
	$F_1$	359.4	207.6	18.1	11.9	4.2
	$F_2$	86.4	43.3	-21.2	-18.9	-17.0

#### RESULTS

Fig. 2 and 3 give plots of the thermodynamic parameters,  $\Delta H_1^\ominus$  and  $\Delta H_f^\ominus(\text{HF}_2^-)(g)$  as functions of  $q_F$ , the charge on the terminal fluorine atoms of the  $\text{HF}_2^-$  ion. The following points emerge: (i) No unique intersection point exists. (ii) The rhombohedral and tetragonal salts exhibit different modes of variation and this can be used as a discriminant, leading to the selection of values:

$$\Delta H_1^\ominus = 176 \pm 6 \text{ kJ mol}^{-1} \quad (30)$$

$$\Delta H_f^\ominus(\text{HF}_2^-)(g) = -728 \pm 9 \text{ kJ mol}^{-1} \quad (31)$$



$$\chi(c) - \Delta H_f^\ominus(M^+)(g) = \sum_{i=0}^2 E_i q_i^c \quad (24)$$

$$-\Delta H_f^\ominus(M^+)(g) \quad (25)$$

$$(26)$$

LENGTH  $\Delta H_f^\ominus$

+ F<sup>-</sup>(g)

oxygen bond in the bifluoride ion.

$$\frac{1}{F} \quad (27)$$

$$+ \Delta H_f^\ominus(HF)(g) + \Delta H_f^\ominus(MF)(c) \quad (28)$$

$$\chi_i \quad (29)$$

$\chi(g) = -271.1 \text{ kJ mol}^{-1}$ , was taken employed are cited in the tables.

ENTHALPIES (units in kJ mol<sup>-1</sup>)

HF <sub>2</sub>	RbHF <sub>2</sub>	CsHF <sub>2</sub>	notes
120.4	-909.2	-904.2	ref. (3)
514.2	494.9	460.6	ref. (31)
769.4	-759.0	-739.1	
18.1	-11.9	-4.2	eqn (25)
21.2	18.9	17.0	
300	765	734	ref. (32)
562.8	-551.5	-545.2	ref. (33)
218.8	204.0	193.7	
18.1	11.9	4.2	eqn (28)
-21.2	-18.9	-17.0	

S

c parameters,  $\Delta H_f^\ominus$  and  $\Delta H_f^\ominus(HF_2)(g)$  fluorine atoms of the HF<sub>2</sub><sup>-</sup> ion. The reaction point exists. (ii) The rhomboides of variation and this can be used values:

$$\pm 6 \text{ kJ mol}^{-1} \quad (30)$$

$$8 \pm 9 \text{ kJ mol}^{-1} \quad (31)$$

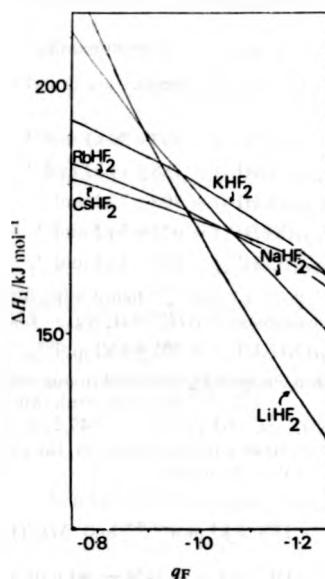


FIG. 2.— $\Delta H_f$  as a function of  $q_F$ .

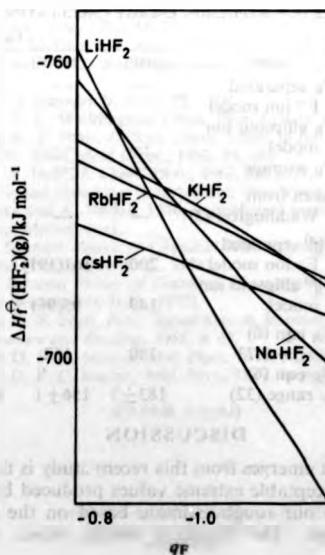


FIG. 3.— $\Delta H_f^\ominus(HF_2)$  as a function  $q_F$ .

with

$$-0.87 \geq q_F \geq -1.05 \text{ proton units.} \quad (32)$$

(iii) The corresponding lattice potential energies are found to be (taking an average  $q_F$  value =  $-0.97$  proton units):

$$U_{\text{POT}}(\text{LiHF}_2) = 893 \pm 20 \text{ kJ mol}^{-1} \quad (33)$$

$$U_{\text{POT}}(\text{NaHF}_2) = 788 \pm 14 \text{ kJ mol}^{-1} \quad (34)$$

$$U_{\text{POT}}(\text{KHF}_2) = 703 \pm 7 \text{ kJ mol}^{-1} \quad (35)$$

$$U_{\text{POT}}(\text{RbHF}_2) = 674 \pm 5 \text{ kJ mol}^{-1} \quad (36)$$

$$U_{\text{POT}}(\text{CsHF}_2) = 646 \pm 4 \text{ kJ mol}^{-1}. \quad (37)$$

(iv)  $\Delta H_f^\circ(\text{NH}_4\text{HF}_2)(\text{c}) = -802.9 \text{ kJ mol}^{-1}$ ,<sup>30</sup> hence using our data for  $\Delta H_f^\circ(\text{HF}_2)(\text{g})$  from above and our recent estimate,<sup>34</sup>  $\Delta H_f^\circ(\text{NH}_4^+)(\text{g}) = 630.2 \text{ kJ mol}^{-1}$  we obtain:

$$U_{\text{POT}}(\text{NH}_4\text{HF}_2) = 705 \pm 9 \text{ kJ mol}^{-1}. \quad (38)$$

(v) We compare the repulsion energies  $U_R$  obtained in our previous study<sup>3</sup> with those obtained for a charge of  $q_F = -0.73$  (the previous result) and for the range [eqn (32)] from this work (table 3). (vi)  $\Delta H_f^\circ(\text{HF}_2)(\text{aq}) = -649.9 \text{ kJ mol}^{-1}$  is listed in ref. (30) and combined with the formation enthalpy data for the gaseous ion we obtain an estimate of the absolute hydration enthalpy:

$$\Delta H_{\text{abs, hyd}}^\circ(\text{HF}_2)(\text{g}) = -357 \pm 9 \text{ kJ mol}^{-1} \quad (39)$$

taking  $\Delta H_{\text{abs, hyd}}^\circ(\text{H}^+)(\text{g}) = -1100.6 \text{ kJ mol}^{-1}$ ,<sup>35</sup> and  $\Delta H_f^\circ(\text{H}^+)(\text{g}) = 1536 \text{ kJ mol}^{-1}$ , whereupon

$$\Delta H_{\text{conv, hyd}}^\circ(\text{HF}_2)(\text{g}) = -1458 \pm 9 \text{ kJ mol}^{-1}. \quad (40)$$

TABLE 3.—REPULSION ENERGY CALCULATIONS

reference	model	$U_R/\text{kJ mol}^{-1}$				
		LiHF <sub>2</sub>	NaHF <sub>2</sub>	KHF <sub>2</sub>	RbHF <sub>2</sub>	CsHF <sub>2</sub>
Waddington (2)	$U_R$ separated F <sup>-</sup> ion model	—	—	154	149	118
	$U_R$ ellipsoid ion model	—	—	122	99	89
	$U_R$ average	—	—	138	124	103
	taken from Waddington (2)	—	—	138	124	103
Neckel, Kuzmany and Vinek (7)	$U_R^{(a)}$ separated F <sup>-</sup> ion model	200	161(191)	146	134	116
	$U_R^{(b)}$ ellipsoid ion model	149	95(96)	111	99	82
	$U_R$ eqn (6)	180	152	109	103	98
Jenkins and Pratt (-0.87 $\geq q_F \geq -1.05$ )	$q_F = -0.73$	180	152	109	103	98
	$U_R$ eqn (6)	183 $\pm$ 1	156 $\pm$ 1	118 $\pm$ 4	110 $\pm$ 3	103 $\pm$ 3
	$q_F$ range (32)	183 $\pm$ 1	156 $\pm$ 1	118 $\pm$ 4	110 $\pm$ 3	103 $\pm$ 3

## DISCUSSION

The obvious point that emerges from this recent study is that  $\Delta H_f^\circ$  is now almost mid-range between the acceptable extreme values produced by quantum mechanical studies and also close to our rough estimate based on the Harrel and McDaniel measured enthalpy change. The repulsion energy, which we claim to be more



proton units. (32)

gies are found to be (taking an average

$3 \pm 20 \text{ kJ mol}^{-1}$  (33)

$8 \pm 14 \text{ kJ mol}^{-1}$  (34)

$3 \pm 7 \text{ kJ mol}^{-1}$  (35)

$4 \pm 5 \text{ kJ mol}^{-1}$  (36)

$6 \pm 4 \text{ kJ mol}^{-1}$ . (37)

hence using our data for  $\Delta H_f^\ominus(\text{HF}_2)(\text{g})$

$2(\text{NH}_4^+)(\text{g}) = 630.2 \text{ kJ mol}^{-1}$  we obtain:

$5 \pm 9 \text{ kJ mol}^{-1}$ . (38)

obtained in our previous study<sup>3</sup> with those

vious result) and for the range [eqn (32)]

$\Delta H_f^\ominus(\text{H}^+)(\text{g}) = -649.9 \text{ kJ mol}^{-1}$  is listed in ref. (30)

data for the gaseous ion we obtain an

$57 \pm 9 \text{ kJ mol}^{-1}$  (39)

$^{1,3,5}$  and  $\Delta H_f^\ominus(\text{H}^+)(\text{g}) = 1536 \text{ kJ mol}^{-1}$ ,

$1458 \pm 9 \text{ kJ mol}^{-1}$ . (40)

## ENERGY CALCULATIONS

$U_n/\text{kJ mol}^{-1}$				
$\text{LiHF}_2$	$\text{NaHF}_2$	$\text{KHF}_2$	$\text{RbHF}_2$	$\text{CsHF}_2$
—	—	154	149	118
—	—	122	99	89
—	—	138	124	103
—	—	138	124	103
200	161(191)	146	134	116
149	95(96)	111	99	82
180	152	109	103	98
$183 \pm 1$	$156 \pm 1$	$118 \pm 4$	$110 \pm 3$	$103 \pm 3$

## DISCUSSION

is recent study is that  $\Delta H_f^\ominus$  is now almost values produced by quantum mechanical rate based on the Harrel and McDaniel on energy, which we claim to be more

reliable than the previous estimates, lies comfortably between the extremes set by our previous two models for the  $\text{HF}_2^-$  ion<sup>3,4</sup> and are lower than values adopted in other studies,<sup>2,7</sup> (table 3). The increased electron density on the terminal fluorine atoms, the dispersion contribution to  $U_{\text{TOT}}$  and the decreased repulsion energy all combine to produce lattice energies for the bifluoride, which are substantially higher than previous estimates, and consequently lower values for  $\Delta H_f^\ominus$ . Hydration data are close to that for the  $\text{N}_3^-$  ion.

Eqn (6) appears to apply successfully to these salts as well as to the azides.

The S.R.C. is thanked for a Studentship to one of us (K. F. P.).

<sup>1</sup> D. F. C. Morris and E. J. Short, *Nature*, 1969, 224, 950.

<sup>2</sup> T. C. Waddington, *Trans. Faraday Soc.*, 1958, 54, 25.

<sup>3</sup> H. P. Dixon, H. D. B. Jenkins and T. C. Waddington, *J. Chem. Phys.*, 1972, 57, 4388.

<sup>4</sup> H. D. B. Jenkins and T. C. Waddington, *J. Chem. Phys.*, 1975, 62, 4586.

<sup>5</sup> M. L. Huggins, *J. Chem. Phys.*, 1937, 5, 143.

<sup>6</sup> J. E. Mayer, *J. Chem. Phys.*, 1933, 1, 270.

<sup>7</sup> A. Neckel, P. Kuzmany and G. Vinek, *Z. Naturforsch.*, 1971, 26a, 569.

<sup>8</sup> G. Bessis and S. Bratoz, *J. Chim. phys.*, 1960, 57, 789.

<sup>9</sup> A. D. McLean and M. Yoshimine, *Int. J. Quantum Chem.*, 1967, 1S, 313.

<sup>10</sup> P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, 1970, 92, 6101.

<sup>11</sup> P. N. Noble and R. N. Kurtzeborn, *J. Chem. Phys.*, 1970, 52, 5375.

<sup>12</sup> J. Almlöf, *Chem. Phys. Letters*, 1972, 17, 49.

<sup>13</sup> J. N. Spencer, G. J. Casey Jnr., J. Buckfelder and H. D. Schreiber, *J. Phys. Chem.*, 1974, 78, 1415.

<sup>14</sup> A. Stogard, A. Strich, J. Almlöf and B. Roos, *Chem. Phys.*, 1975, 8, 405.

<sup>15</sup> P. Schuster, G. Zundel and C. Sandorfy, *The Hydrogen Bond, Vol. 1 Theory* (North Holland, Amsterdam, 1976).

<sup>16</sup> W. S. Fyfe, *J. Chem. Phys.*, 1953, 21, 2.

<sup>17</sup> M. Davies, *J. Chem. Phys.*, 1947, 15, 739.

<sup>18</sup> A. S. N. Murphy, S. N. Bhat and C. N. R. Rao, *J. Chem. Soc. A*, 1970, 1251.

<sup>19</sup> P. Schuster, *Theor. Chim. Acta*, 1970, 19, 212.

<sup>20</sup> S. A. Harrel and D. H. McDaniel, *J. Amer. Chem. Soc.*, 1969, 86, 4497.

<sup>21</sup> C. Thomson, D. T. Clark, T. C. Waddington and H. D. B. Jenkins, *J.C.S. Faraday II*, 1975, 71, 1942.

<sup>22</sup> H. D. B. Jenkins, *J.C.S. Faraday II*, 1976, 72, 1569.

<sup>23</sup> H. D. B. Jenkins and T. C. Waddington, *Chem. Phys. Letters*, 1975, 31, 369.

<sup>24</sup> H. D. B. Jenkins and K. F. Pratt, *J. Phys. Chem. Solids*, in the press.

<sup>25</sup> L. K. Frevel and H. W. Rinn, *Acta Cryst.*, 1962, 15, 286.

<sup>26</sup> B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, 1963, 39, 2677.

<sup>27</sup> R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 2nd edn., 1964).

<sup>28</sup> P. Herzig, P. Kuzmany and A. Neckel, 1970, unpublished work.

<sup>29</sup> K. F. Pratt, 1976, unpublished work.

<sup>30</sup> V. B. Parker *et al.*, *Selected Values of Chemical Thermodynamic Properties* (Technical Note 270-3, Nat. Bur. Stand. Washington D.C., 1971).

<sup>31</sup> F. D. Rossini *et al.*, *Selected Values of Chemical Thermodynamic Properties* (N.B.S. Circular 500, Nat. Bur. Stand. Washington D.C., 1952).

<sup>32</sup> H. D. B. Jenkins and K. F. Pratt, *Proc. Royal Soc. A*, in press.

<sup>33</sup> D. F. C. Morris, *Structure and Bonding*, 1968, 4, 63.

<sup>34</sup> H. D. B. Jenkins and D. F. C. Morris, *Mol. Phys.*, 1976, 32, 231.

<sup>35</sup> H. D. B. Jenkins and D. F. C. Morris, *Mol. Phys.*, 1977, in press.

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## CALCULATION OF THE FIRST DERIVATIVES OF MADELUNG CONSTANTS WITH RESPECT TO CELL LENGTHS

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University of Warwick, Coventry, W. Midlands, CV4 7AL, UK

Received 23 May 1977

### PROGRAM SUMMARY

*Title of program:* MADELUNG DERIVATIVES

*Catalogue number:* ACMO

*Program obtainable from:* CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue).

*Computer:* B6700; *Installation:* Computer Centre, University of Warwick, Coventry, W. Midlands, CV4 7AL.

*Operating system:* Master Control Program

*Programming language used:* FORTRAN IV

*High speed storage required:* 6 500 words

*No. of bits in a word:* 48

*Overlay structure:* none

*No. of magnetic tapes required:* none

*Other peripherals used:* card reader lineprinter and/or on-line terminal

*No. of cards in combined program and test deck:* 1099

*Card punching code:* EBCDIC

*Reference to other published version of this program:* QCPE Program 222

*Keywords:* Solid state physics, Madelung constant, Madelung

derivatives, Bertaut method, Fourier transform, complex ion, self energy.

#### *Nature of physical problem*

To calculate the Madelung constant and its derivatives with respect to the cell lengths for the input crystal structure, in a charge dependent and charge independent form.

#### *Method of solution*

The Madelung constant is calculated by the use of the Bertaut [1] approach. This is differentiated term by term to obtain the derivatives with respect to the cell lengths. Complex ions can be treated as entities having fixed geometry and if this is done their self energy may be calculated.

#### *Restriction on the complexity of the problem*

The cut-off radius of the charge-density function must be chosen as cell length independent. If a Gaussian charge-density function is used and an overlap correction is required then derivatives will not be calculated.

#### *Typical running time*

For sodium nitrite ( $\text{NaNO}_2$ ) [2] with convergence to six decimal places [3]—1000 s.

*Unusual features of the program:* none

#### *References*

- [1] E.F. Bertaut, J. Phys. Radium 13 (1952) 499.
- [2] M.I. Kay and B.C. Frazer, Acta Cryst. 14 (1961) 56.
- [3] H.D.B. Jenkins, Chem. Phys. Lett. 9 (1971) 473; 20 (1973) 155;  
H.D.B. Jenkins, J. Chem. Soc. Faraday II, 72 (1976) 1569.

## LONG WRITE-UP

## 1. Introduction

The necessary theory for constructing first derivatives of a Madelung constant with respect to the cell lengths is summarised. Once obtained these derivatives yield the equivalent derivatives of the electrostatic energy of the crystal lattice. The theory allows for the retention of geometry of complex ions in going from the gaseous to the solid state. The program described is based on a program written by Blake (Hull) [1] to calculate Madelung constants, adapted by HDBJ to use Bertaut's method [2] and further adapted by Smith (formerly of Warwick) [3] to give the Madelung interaction between each pair of atom types in the structure, hence giving the overall Madelung constant as a function of the distribution of charge over the atoms.

The program is generally applicable except when a Gaussian charge-density function is chosen, this may require an overlap correction and then derivatives are not calculated.

## 2. Theory

An outline of the Bertaut method [2] of calculating Madelung constants is given and it is indicated how this is a function of the cell lengths, showing how the expression may be differentiated with respect to the cell lengths.

Bertaut has shown [2] that the Madelung constant can be expressed by:

$$M_1 = \frac{g}{R\mu} \sum_{j=1}^N n_j q_j^2 - \frac{1}{\mu 2\pi V} \sum_h \sum_k \sum_l \frac{|F_{hkl}|^2 \phi_{hkl}^2}{S_{hkl}^2} \quad (1)$$

where

- $M_1$  = the Madelung constant based on unit distance,
- $g$  = a constant dependent on which charge-density function is used,
- $R$  = the cut-off radius of the charge-density function,
- $\mu$  = the number of molecules per unit cell,
- $n_j$  = the number of the  $j$ th type of atom in the unit cell,
- $q_j$  = the charge on the  $j$ th type of atom,
- $N$  = the total number of types of atom,
- $h, k, l$  = reciprocal unit cell indices,

$V$  = the unit cell volume given by

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}, \quad (2)$$

where

$a, b, c$  = the cell lengths,

$\alpha, \beta, \gamma$  = the cell angles,

$S_{hkl}^2$  = the square of the reciprocal lattice vector and is given by:

$$S_{hkl}^2 = \frac{1}{V^2} \left[ h^2 b^2 c^2 \sin^2 \alpha + k^2 c^2 a^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma + \frac{2hkabc^2(\cos \alpha \cos \beta - \cos \gamma)}{\sin \alpha \sin \beta} + \frac{2kla^2 bc(\cos \beta \cos \gamma - \cos \alpha)}{\sin \beta \sin \gamma} + \frac{2lhab^2 c(\cos \gamma \cos \alpha - \cos \beta)}{\sin \gamma \sin \alpha} \right], \quad (3)$$

$\phi_{hkl}^2$  = the square of the Fourier transform of the charge-density function, given by Templeton [4], and is a function of  $R$  and  $S_{hkl}^2$ .

$|F_{hkl}|^2$  = the square of the modulus of the coulombic structure factor and is given by:

$$|F_{hkl}|^2 = \left\{ \sum_{i=1}^N q_i \sum_{j=1}^{n_i} \cos(ARG_{ij}) \right\}^2 + \left\{ \sum_{i=1}^N q_i \sum_{j=1}^{n_i} \sin(ARG_{ij}) \right\}^2, \quad (4)$$

where

$$ARG_{ij} = 2\pi \{hx_{ij} + ky_{ij} + lz_{ij}\}, \quad (5)$$

where  $x_{ij}, y_{ij}, z_{ij}$  are the fractional coordinates of the atom designated  $ij$ .

It can be seen from eq. (3) that  $S_{hkl}^2$  is easily differentiated with respect to the cell lengths, as is  $V$  [eq. (2)], and hence so is  $\phi_{hkl}^2$  as this is independent of the cell lengths apart from its dependence on  $S_{hkl}^2$ . Considering eqs. (4) and (5) it would appear at first sight that the coulombic structure factor is independent of the cell constants. However if an atom, in a complex ion, is to have a fixed position relative to the central atom in the

$V$  = the unit cell volume given by

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}, \quad (2)$$

where

$a, b, c$  = the cell lengths,

$\alpha, \beta, \gamma$  = the cell angles,

$S_{hkl}^2$  = the square of the reciprocal lattice vector and is given by:

$$S_{hkl}^2 = \frac{1}{V^2} \left[ h^2 b^2 c^2 \sin^2 \alpha + k^2 c^2 a^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma + \frac{2hkabc^2(\cos \alpha \cos \beta - \cos \gamma)}{\sin \alpha \sin \beta} + \frac{2kla^2 bc(\cos \beta \cos \gamma - \cos \alpha)}{\sin \beta \sin \gamma} + \frac{2lhab^2 c(\cos \gamma \cos \alpha - \cos \beta)}{\sin \gamma \sin \alpha} \right], \quad (3)$$

$S_{hkl}^2$  = the square of the Fourier transform of the charge-density function, given by Templeton [4], and is a function of  $R$  and  $S_{hkl}^2$ .

$|S_{hkl}|^2$  = the square of the modulus of the coulombic structure factor and is given by:

$$|S_{hkl}|^2 = \left\{ \sum_{i=1}^N q_i \sum_{j=1}^{n_i} \cos(ARG_{ij}) \right\}^2 + \left\{ \sum_{i=1}^N q_i \sum_{j=1}^{n_i} \sin(ARG_{ij}) \right\}^2, \quad (4)$$

where

$$RG_{ij} = 2\pi \{hx_{ij} + ky_{ij} + lz_{ij}\}, \quad (5)$$

where  $x_{ij}, y_{ij}, z_{ij}$  are the fractional coordinates of the atom designated  $ij$ .

It can be seen from eq. (3) that  $S_{hkl}^2$  is easily differentiated with respect to the cell lengths, as is  $V$  [eq. (2)], and hence so is  $\phi_{hkl}^2$  as this is independent of the cell lengths apart from its dependence on  $S_{hkl}^2$ . Considering eqs. (4) and (5) it would appear at first sight that the coulombic structure factor is independent of the cell constants. However if an atom, in a complex ion, is to have a fixed position relative to the central atom in the

ion its fractional coordinates must be expressed:

$$(x + d_x/a, y + d_y/b, z + d_z/c), \quad (6)$$

where  $x, y, z$  are the fractional coordinates of the central atom (or position if no atom is central) of the complex ion and  $d_x, d_y, d_z$  are the distances in the  $x, y, z$  directions of the terminal atom away from the central atom, these are the parameters which must remain constant with changes in  $a, b$  and  $c$ . Eq. (5), with these coordinates, is now cell constant dependent and has non-zero calculable derivatives, and consequently so does eq. (4).

The same approach is used to calculate the Madelung interactions between pairs of individual atom types. Considering eqs. (1) and (4) it can be seen that simple division of these terms by the charge on each type of atom gives charge independent terms where:

$$M_i = \sum_{j=1}^N \sum_{l=1}^{n_j} I_{ij} q_l q_j, \quad (7)$$

where  $I_{ij}$  are the charge independent terms.

A range of charge-density functions can be used in the program; uniform, linear, parabolic and Gaussian. All but the Gaussian function are designed to collapse to a zero charge density at distances greater than a pre-determined distance from the atomic centre. This distance must be less than or equal to half the shortest interatomic distance in the unit cell. It takes the value of half the shortest distance in the current listing but may be varied if desired. However the calculation of derivatives assumes that the distance is cell length independent and if it does not represent an internal distance of a complex ion an appropriate (constant) value should be input. For the Gaussian charge-density function overlap between atoms is unavoidable and although normally small it is necessary to calculate a correction term. In such cases derivatives are not calculated by the program.

In the program total isotropic derivatives are calculated, i.e. the unit cell symmetry is retained and for cubic and rhombohedral symmetries only one total derivative with respect to  $a$  (at  $a = a_0$ ) is calculated, for tetragonal and hexagonal symmetries one with respect to  $a$  (at  $a = a_0$ ) and one with respect to  $c$  (at  $c = c_0$ ) and for orthorhombic, monoclinic and triclinic derivatives with respect to  $a$  (at  $a = a_0$ ),  $b$  (at  $b = b_0$ ) and  $c$  (at  $c = c_0$ ) are calculated.

The program also calculates the self energies of individual complex ions in the unit cell, using the relationship:

$$U_{SE} = \frac{1}{2} K \sum_{i=1}^m \sum_{j=1, j \neq i}^m q_i q_j / r_{ij}, \quad (8)$$

where

$U_{SE}$  = the self energy.

$K$  = a conversion factor,

$m$  = the number of atoms in the complex ion,

$r_{ij}$  = the distance between atom  $i$  and atom  $j$ .

The self energy is calculated as a function (quadratic) of the charge on the terminal (outer) atoms of the complex ion.

### 3. Description of program

#### 3.1. Program MADELUNG DERIVATIVES:

This is the main body of the program, which executes the major summation, inputs the data and outputs the majority of the results.

The summation is carried out by incrementing  $|h|$  starting at 0 and for each value adopting values of  $k$  and  $l$  consistent with the requirement that the reciprocal lattice vector should be less than the maximum permitted length (pre-set). By considering the symmetry of the lattice the program determines whether terms are systematically absent prior to calculation and avoids the duplicate calculation of equivalent terms. It calculates the Madelung constant as a single value and as individual sums between pairs of atom types, together with the necessary derivatives.

The results are output both in their charge dependent and charge independent forms.

If required, the self energies of individual complex ions are calculated and output as functions of the charge on the terminal atoms.

#### 3.2. Subroutine DIST

If called, this subroutine computes all the interatomic distances in the unit cell, taking the distance corresponding to an adjacent cell if this is shorter. These values can be output if required. In this way it finds the short-

test interatomic distance which is used to determine the fourier transform of the charge-density function. It also calculates the Gaussian overlap correction term if required.

The parameters are used as follows:

- NOVLAP = is a pointer to indicate whether the Gaussian overlap correction term is required,  
 EOVLAP = is used to return the Gaussian overlap correction term,  
 NDCALC = indicates if a table of interatomic distances should be output or not,  
 RMIN = is used to return the shortest interatomic distance,  
 RSQMIN = is used to return the square of the shortest interatomic distance.

### 3.3. Real function SHAPE

This returns the value of  $g/R$  in eq. (1). The parameters are used as follows:

- NSHAPE = indicates which charge-density function is being used,  
 RMIN = is the cut-off value for the charge-density function.

### 3.4. Real function PHISQD

This returns the value of the square of the fourier transform of the charge-density function. The parameters are used as follows:

- NSHAPE = indicates which charge-density function is being used,  
 RSQMIN = is the square of the cut-off value for the charge-density function,  
 SSQD = is the square of the reciprocal lattice vector.

### 3.5. Real function DPHSQD

This returns the value of  $\partial\phi_{hkl}^2/\partial S_{hkl}^2$ . The parameters are as given above.

All distances input to the program should be in Angstroms, the Madelung constants output will then be in reciprocal Angstroms and the energies in kilojoules per mole.

## 4. Input Data

### CARD 1 (I2)

- 1 - NJOBS the number of jobs to be run in this data deck.

### CARD 2 (12A6)

- 1 - TITLE 72 character alphanumeric title.

### CARD 3 (3F9.6)

- 1 - A cell length  $a_0$ ,  
 2 - B cell length  $b_0$ ,  
 3 - C cell length  $c_0$ .

### CARD 4 (3F9.6)

- 1 - COSA cosine of cell angle  $\alpha$ ,  
 2 - COSB cosine of cell angle  $\beta$ ,  
 3 - COSC cosine of cell angle  $\gamma$ .

### CARD 5 (I2)

- 1 - NMOLS number of molecules per unit cell.

### CARD 6(A1, 2X, I1)

- 1 - BRAV unit cell symmetry.  
 P(primitive), A,B,C(a, b, c centered), I(body centered), F(face centered), R(trigonally centered).  
 0 if centrosymmetric, 1 if non-centrosymmetric.

- 2 - ICENT

### CARD 7 (I2)

- 1 - NDIFKN number of different kinds of ion, complex ions counted as one.

Cards 8-10 are repeated NDIFKN times.

### Card 8 (2(A2, 2X, I2, 2X, F6.3, 2X))

- 1 - SYM two letter symbol of central atom of the ion,  
 2 - NEACH number of this type of ion,  
 3 - Q charge on the central atom (non-zero),  
 4 - ASYM two letter symbol of terminal atoms of complex ion, blank if not complex,  
 5 - NASS number of terminal atoms of the complex ion,  
 6 - QD charge on the terminal atoms (non-zero if complex ion).

Card 9 is repeated NEACH times.

### CARD 9 (3F6.4, I2)

- 1 - X } fractional coordinates of the  
 2 - Y } central atom  
 3 - Z }  
 4 - SET set of relative coordinates of terminal atoms associated with this

## Data

1 (I2)  
NJOBS the number of jobs to be run in this data deck.

2 (I2A6)  
TITLE 72 character alphanumeric title.

3 (3F9.6)  
A cell length  $a_0$ ,  
B cell length  $b_0$ ,  
C cell length  $c_0$ .

4 (3F9.6)  
COSA cosine of cell angle  $\alpha$ ,  
COSB cosine of cell angle  $\beta$ ,  
COSC cosine of cell angle  $\gamma$ .

5 (I2)  
NMOLS number of molecules per unit cell.

6(A1, 2X, I1)  
BRAV unit cell symmetry, P(primitive), A, B, C( $a$ ,  $b$ ,  $c$  centered), I(body centered), F(face centered), R(trigonally centered), 0 if centrosymmetric, 1 if non-centrosymmetric.

ICENT

7 (I2)  
NDIFKN number of different kinds of ion, complex ions counted as one.

10 are repeated NDIFKN times.

(2(A2, 2X, I2, 2X, F6.3, 2X))  
SYM two letter symbol of central atom of the ion,

NEACH number of this type of ion,

Q charge on the central atom (non-zero),

ASYM two letter symbol of terminal atoms of complex ion, blank if not complex,

NASS number of terminal atoms in the complex ion,

QD charge on the terminal atoms (non-zero if complex ion).

is repeated NEACH times.

9 (3F6.4, I2)  
X } fractional coordinates of the  
Y } central atom  
Z }

SET set of relative coordinates of terminal atoms associated with this

central atom (zero if not complex)  
(1 first, then 2 etc.).

Card 10 is repeated NASS times for each SET (see above), i.e. not present if not complex.

## CARD 10 (3F6.4)

1 - XD

2 - YD

fractional coordinates of terminal atom relative to a central atom,

3 - ZD

## CARD 11 (3I2)

1 - NH

2 - NK

3 - NL

sign reversal symmetry of  $|F_{hkl}|$ :  
1, 1, 0 if  $|F_{hkl}|$  depends on the signs of  $h$  and  $k$  but not  $l$  (i.e. monoclinic with  $c$ -axis unique, hexagonal and tetragonal space groups 75-88); 0, 0, 0 if  $|F_{hkl}|$  is independent of signs of  $h$ ,  $k$  and  $l$  (i.e. orthorhombic, cubic and tetragonal space groups 89-142); 1, 1, 1 if  $|F_{hkl}|$  depends on signs of  $h$ ,  $k$  and  $l$  (i.e. triclinic and trigonal space groups or if in doubt).

## CARD 12 (3I2)

1 - LH

2 - LK

3 - LL

permutation symmetry of  $|F_{hkl}|$ :  
1, 1, 0 if  $h$  and  $k$  interchangeable (i.e. tetragonal space groups 89-142); 1, 1, 1 if  $h$ ,  $k$  and  $l$  are permutable (other than cyclically) (i.e. certain trigonal and cubic space groups - 160, 166, 215-7, 221, 224-5, 227 and 229); 0, 0, 0 if no index pairs are reversible (or if in doubt).

## CARD 13 (2I2)

1 - NSHAPE

form of charge-density function:  
0 uniform, 1 linear; 2 parabolic;  
3 Gaussian.

2 - NOV LAP

1 if NSHAPE = 3 and overlap energy correction required, 0 otherwise.

## CARD 14 (I2, F9.6)

the shortest distance is twice the charge-density function cut-off radius,

1 - NDCALC

0 if calculation of the shortest interatomic distance is not required ( $D$  must be specified). Used if the distance is known or the shortest distance is not cell length independent; -1 if shortest interatomic

distance is to be calculated and a table of all interatomic distances is to be output; 1 if shortest interatomic distance is to be calculated. Non-zero distance if NDCALC = 0, must be less than or equal to the shortest distance (N.B. on a multiple run on the same structure calculate  $D$  on the first run and on successive runs put NDCALC = 0 and  $D = 0.0$ , original value is retained).

2 - D

## CARD 15 (F6.2)

1 - SSQMAX

maximum length of reciprocal lattice vector squared to be included in the summation (estimated by the method of Jenkins [5]).

## CARD 16 (I2)

1 - NPRINT

1 if a print-out of the individual terms in the summation is required (N.B. this produces a very large amount of print-out and should be avoided): 0 if this print-out is not required (usual).

## CARD 17 (E7.1)

1 - EPS

largest error tolerable in the summation.

## CARD 18 (I2)

1 - NSELF

1 if self energies of the complex ions are required, 0 if not.

## 5. Description of Output

The first page of output is the crystal structure; cell dimensions, unit cell volume, cell symmetry and fractional coordinates of all the atoms.

The next page(s), if this is requested, give a table of the interatomic distances, consisting of the fractional coordinates of the atoms, their position in the table of coordinates and the shortest distance between the two.

Following this is output the shortest distance (or the distance input as the shortest distance), what type of charge-density function has been selected and its range, the maximum reciprocal lattice vector squared and the accuracy parameter (EPS, see section 4).

If requested, the following pages give a table of the individual terms for each unit cell considered. For a realistic maximum reciprocal lattice vector this would be a vast amount of lineprinter output, but for small values (less than  $1 \text{ \AA}^{-1}$ ) the short table produced can be diagnostically useful.

After the summation is complete the results are output in various forms. The 'total energy term' is the value obtained by the main summation and the 'interaction energy' is this value when corrected by the 'atomic' 'self energy term'. The derivatives of the 'interaction energy' are output below this. The Madelung energy, in kJ/mol, for the input charge distribution is output next followed by the Madelung constants based on various distances (the shortest distance and different cell lengths) with their appropriate derivatives. Below this is output the constituent terms of the Madelung constant based on unit distance, these terms divided by the appropriate charges ( $Q \text{ DEP}$ ) [i.e.  $I_{ij}$ , eq. (7)] and the terms  $J_{ij}$  defined by:

$$\frac{\partial M_i}{\partial x} = \sum_{j=1}^N \sum_{k=1}^N J_{ijk} \frac{\partial q_j}{\partial x}, \quad (9)$$

where  $x = a, b, c$  when appropriate.

The table entitled 'convergence indication' shows the value of the 'total energy term' before  $|h|$  is incremented. This is not an absolute measure of convergence, if no change is shown over several terms convergence could have been achieved, but if the 'total energy term' is still increasing convergence, to any degree of accuracy, has not been achieved.

On the last page the self energy of the complex ions are output as functions of the charge on the terminal atoms, the chemical symbols being used as a guide. Each different input set of complex ion coordinates (see section 4) will have a self energy output. If no complex ions exist in the structure but self energy calculations are requested, a message to that effect is output.

## 6. Description of the test run

As an example of the use of this program a body centered, orthorhombic form of sodium nitrite [6] was chosen because: (i) it has a relatively small unit cell; (ii) it has a complex ion; (iii)  $a \neq b \neq c$  and so three derivatives are calculated by the program. The full

structure is given in the output shown. A parabolic charge-density function is chosen with a range of half the shortest interatomic distance calculated by the program (a N—O distance and so a constant with respect to the cell lengths). The maximum reciprocal lattice vector is set at  $10 \text{ \AA}^{-1}$  (calculated by the method of Jenkins [5]) to give convergence to six decimal places. The table of interatomic distances is output but the individual terms in the summation are not. The accuracy parameter is set low at  $0.5 \times 10^{-10}$ . The self energy of the one type of nitrite ion is calculated.

Results obtainable from this run of the program are (in kJ/mol and kJ/mol/Å):

$$U_{\text{ELEC}}(\text{NaNO}_2) = 782.8 + 3.8 q_0 + 117.1 q_0^2, \quad (10)$$

$$\left( \frac{\partial U_{\text{ELEC}}(\text{NaNO}_2)}{\partial a} \right)_d = 3.6 + 101.4 q_0 - 6.1 q_0^2, \quad (11)$$

$$\left( \frac{\partial U_{\text{ELEC}}(\text{NaNO}_2)}{\partial b} \right)_d = -81.8 - 82.0 q_0 - 42.4 q_0^2, \quad (12)$$

$$\left( \frac{\partial U_{\text{ELEC}}(\text{NaNO}_2)}{\partial c} \right)_d = -63.2 + 8.0 q_0 - 30.1 q_0^2, \quad (13)$$

where

$U_{\text{ELEC}}$  = the electrostatic energy of the lattice;  
 $d$  = the N—O bond length in the nitrite ion;  
 $q_0$  = the charge on the oxygen atoms.

## Acknowledgements

We would like to thank Dr. A.B. Blake (Hull) for valuable discussions during this work. KFP acknowledges the provision of a Science Research Council Studentship.

## References

- [1] A.B. Blake, Quantum Chemistry Program Exchange, Program 222, Indiana Univ., (1973).
- [2] S.F. Bertaut, J. Phys. Radium 13 (1952) 499.
- [3] B.T. Smith, unpublished work.
- [4] D.H. Templeton, J. Chem. Phys. 23 (1955) 1629.
- [5] H.D.B. Jenkins, Chem. Phys. Lett. 9 (1971) 473; 20 (1973) 155.
- [6] M.I. Kay and B.C. Frazer, Acta Cryst. 14 (1961) 56.



is given in the output shown. A parabolic density function is chosen with a range of half the interatomic distance calculated by the N—O distance and so a constant with the cell lengths). The maximum reciprocal factor is set at  $10 \text{ \AA}^{-1}$  (calculated by the Jenkins [5]) to give convergence to six dec. The table of interatomic distances is outside individual terms in the summation are accuracy parameter is set low at  $0.5 \times 10^{-10}$  energy of the one type of nitrite ion is calcu-

s obtainable from this run of the program are  $\Delta$  and kJ/mol/Å):

$$\Delta(\text{NaNO}_2) = 782.8 + 3.8 q_0 + 117.1 q_0^2, \quad (10)$$

$$\left( \frac{\Delta(\text{NaNO}_2)}{\Delta a} \right)_d = 3.6 + 101.4 q_0 - 6.1 q_0^2, \quad (11)$$

$$\left( \frac{\Delta(\text{NaNO}_2)}{\Delta b} \right)_d = -81.8 - 82.0 q_0 - 42.4 q_0^2, \quad (12)$$

$$\left( \frac{\Delta(\text{NaNO}_2)}{\Delta c} \right)_d = -63.2 + 8.0 q_0 - 30.1 q_0^2, \quad (13)$$

$\Delta$  = the electrostatic energy of the lattice;  
 $a$  = the N—O bond length in the nitrite ion;  
 $q$  = the charge on the oxygen atoms.

## Acknowledgements

We would like to thank Dr. A.B. Blake (Hull) for discussions during this work. KFP acknowledges the award of a Science Research Council Studentship.

References

- Blake, Quantum Chemistry Program Exchange, Proc. 222, Indiana Univ., (1973).
- Bertaut, J. Phys. Radium 13 (1952) 499.
- Smith, unpublished work.
- Templeton, J. Chem. Phys. 23 (1955) 1629.
- B. Jenkins, Chem. Phys. Lett. 9 (1971) 473; 20 (1973) 56.
- Kay and B.C. Frazer, Acta Cryst. 14 (1961) 56.

## TEST RUN OUTPUT

SODIUM NITRITE - CPC TEST DATA			
CELL DIMENSIONS			
A = 3.5690	COS ALPHA = 0.0000		
B = 5.5630	COS BETA = 0.0000		
C = 5.5640	COS GAMMA = 0.0000		
UNIT CELL VOLUME = 106.8956			
UNIT CELL IS I-CENTRED AND NON-CENTROSYM.			
WITH ORTHORHOMBIC SYMMETRY			
THERE ARE 2 MOLECULES PER UNIT CELL			
FRACTIONAL COORDINATES OF ALL IONS			
CHARGE	NUMBER	SYMBOL	X Y Z
1.00	2	Na	0.0500 3.5853 0.0000
1.00	2	N	0.5000 3.6200 0.5000
-2.00	4	O	0.0000 3.0000 0.1941
			0.0500 3.0000 -0.1941
			0.5000 3.5000 0.6941
			0.5500 3.5000 0.3059
INTER-IONIC DISTANCES			
ION COORDINATES			
ION (A)	ION (B)	DISTANCE	
0.0000 0.5853 0.0000	0.5300 0.5000	4.2624	2
0.0000 0.5853 0.0000	0.0000 0.0000	2.5685	3
0.0000 0.5853 0.0000	0.0000 0.1941	2.5326	4
0.0000 0.5853 0.0000	0.0000 0.6941	2.5326	5
0.0000 0.5853 0.0000	0.5000 0.5000	2.4763	6
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	7
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	8
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	9
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	10
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	11
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	12
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	13
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	14
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	15
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	16
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	17
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	18
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	19
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	20
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	21
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	22
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	23
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	24
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	25
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	26
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	27
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	28
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	29
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	30
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	31
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	32
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	33
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	34
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	35
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	36
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	37
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	38
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	39
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	40
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	41
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	42
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	43
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	44
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	45
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	46
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	47
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	48
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	49
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	50
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	51
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	52
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	53
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	54
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	55
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	56
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	57
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	58
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	59
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	60
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	61
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	62
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	63
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	64
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	65
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	66
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	67
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	68
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	69
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	70
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	71
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	72
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	73
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	74
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	75
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	76
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	77
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	78
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	79
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	80
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	81
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	82
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	83
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	84
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	85
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	86
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	87
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	88
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	89
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	90
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	91
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	92
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	93
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	94
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	95
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	96
0.0000 0.5853 0.0000	0.5000 0.0000	2.4763	97
0.0000 0.5853 0.0000	0.5000 0.1941	2.4763	98
0.0000 0.5853 0.0000	0.5000 0.6941	2.4763	99
0.0000 0.5853 0.0000	0.5000 0.3059	2.4763	100



SHORTEST DISTANCE = 1.2401

CHARGE-DENSITY FUNCTION IS PARABOLIC WITH RANGE 0.6200 ANGSTROMS

SUM INCLUDES ONLY TERMS FOR WHICH S-SQUARED IS LESS THAN 100.00

ACCURACY PARAMETER .5E-13

SODIUM NITRITE - CPC TEST DATA

TOTAL ENERGY TERM = 34.524414  
 SELF ENERGY TERM = 51.841372  
 INTERACTION ENERGY TERM = -17.316554  
 DIFFERENTIAL WRT A = 0.322101  
 DIFFERENTIAL WRT B = 0.126095  
 DIFFERENTIAL WRT C = 0.297352

MADLUNG ENERGY = 12029.617 KJ PER MOLE

MADLUNG CONSTANTS

(1) (SHORTEST DISTANCE) 13.736793  
 DIFFERENTIAL WRT A = -0.199711  
 DIFFERENTIAL WRT B = -0.078162  
 DIFFERENTIAL WRT C = -0.178166  
 (2) (A-EDGE OF UNIT CELL) 33.901577  
 DIFFERENTIAL WRT A = 0.383540  
 (3) (B-EDGE OF UNIT CELL) 48.164285  
 DIFFERENTIAL WRT B = 0.327597  
 (4) (C-EDGE OF UNIT CELL) 46.616446  
 DIFFERENTIAL WRT C = 7.994778

ATOMS	M.C. (UNIT DISTANCE)	Q DEP	DIFF. Q DEP (A)	DIFF. Q DEP (B)	DIFF. Q DEP (C)
NA NA	.373825918E+03	.373825918E+00	-.240344812E-01	-.249040006E-01	-.261697054E-01
NA N	.276262714E+00	.920875715E-01	-.253355143E-01	.454839641E-02	-.341004421E-02
NA O	-.268798561E+03	.134399280E+03	-.145044761E-01	-.411689224E-02	.936813007E-02
N NA	.276262714E+03	.920875715E-01	-.253355143E-01	.454839641E-02	-.341004421E-02
N N	.336443343E+01	.373825918E+00	-.240344812E-01	-.249040006E-01	-.261697054E-01
N O	.659415494E+03	-.109902576E+03	-.484121677E-01	-.335121262E-01	-.393474125E-01
O NA	-.268798561E+03	.134399280E+03	-.145044761E-01	-.411689224E-02	.936813007E-02
O N	.659415494E+03	-.109902576E+03	-.484121677E-01	-.335121262E-01	-.393474125E-01
O O	.398631066E+01	.896577666E+00	-.101914675E-00	-.649776841E-01	-.731517561E-01

CONVERGENCE INDICATION

N	TOTAL ENERGY TERM	N	TOTAL ENERGY TERM
0	11.368384	18	34.524410
1	26.270694	19	34.524411
2	32.028271	20	34.524412
3	33.914991	21	34.524412
4	34.410136	22	34.524413
5	34.507564	23	34.524413
6	34.521112	24	34.524413
7	34.522821	25	34.524413
8	34.523637	26	34.524413
9	34.523890	27	34.524413
10	34.524100	28	34.524413
11	34.524323	29	34.524413
12	34.524365	30	34.524413
13	34.524380	31	34.524413
14	34.524390	32	34.524413
15	34.524399	33	34.524414
16	34.524405	34	34.524414
17	34.524409	35	34.524414

SELF ENERGIES OF THE COMPLEX IONS

N O 2 IOH

SET 1 U(5E) = -2240.709 -3CD 1 = -3816.784 -810 3\*\*2  
 Q(0) = -2.01 U(5E) PREDICTED = -10785.196  
 U(5E) CALCULATED = -10785.196

# SINGLE ION PROPERTIES BY LATTICE ENERGY MINIMISATION THE PERCHLORATE ION, $\text{ClO}_4^-$

P (A)	DIFF. 0 DEP (B)	DIFF. 0 DEP (C)
2E-01	-24904000E-01	-261697054E-01
3E-01	-454839641E-02	-141004421E-02
4E-01	-411689224E-02	-936013007E-02
5E-01	-454839641E-02	-141004421E-02
6E-01	-24904000E-01	-261697054E-01
7E-01	-335121262E-01	-390474125E-01
8E-01	-411689224E-02	-141004421E-02
9E-01	-335121262E-01	-390474125E-01
5E+00	-649776841E-01	-731537961E-01

## INTRODUCTION

The present paper is concerned with the calculation of the single ion properties of the perchlorate ion,  $\text{ClO}_4^-$ , in a crystal lattice. The method used is based on the minimisation of the lattice energy, which is a function of the ionic radii and the dielectric constant of the medium. The results are compared with those obtained from other methods, such as the use of Madelung constants and the Born-Haber cycle. The paper is divided into three main sections: the first describes the method of calculation, the second presents the results for the perchlorate ion, and the third discusses the implications of the findings.

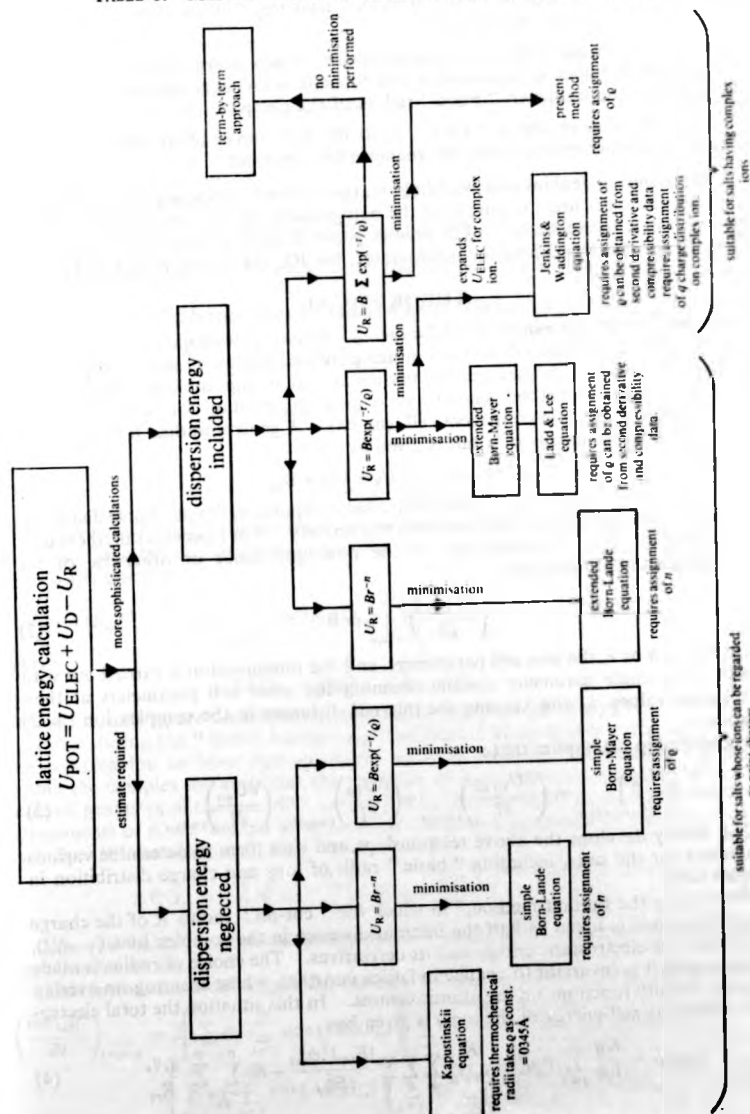
The first section describes the method of calculation. The lattice energy is calculated as a function of the ionic radii and the dielectric constant of the medium. The ionic radii are determined by minimising the lattice energy with respect to the ionic radii. The dielectric constant is determined by minimising the lattice energy with respect to the dielectric constant. The results are compared with those obtained from other methods, such as the use of Madelung constants and the Born-Haber cycle.

The second section presents the results for the perchlorate ion. The ionic radius is found to be 0.249 nm, and the dielectric constant is found to be 2.617. The lattice energy is found to be -261.697 eV. The results are compared with those obtained from other methods, such as the use of Madelung constants and the Born-Haber cycle.

The third section discusses the implications of the findings. The results show that the lattice energy minimisation method is a reliable method for calculating the single ion properties of the perchlorate ion. The results are in good agreement with those obtained from other methods, such as the use of Madelung constants and the Born-Haber cycle.



TABLE 1.—METHODS FOR CALCULATING LATTICE ENERGIES OF SALTS



## Lattice Energy Minimisation

perchlorate ion,  $\text{ClO}_4^-$ 

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basic radii and thermodynamic parameters) may be proposed theory extends current methods of forming minimisation with respect to the individual amount of information that can be obtained from obtain data for the perchlorate ion by consideration We obtain:

- $U_{\text{R}} = 643 \text{ kJ mol}^{-1}$
- $U_{\text{R}} = 599 \text{ kJ mol}^{-1}$
- $U_{\text{R}} = 583 \text{ kJ mol}^{-1}$
- $U_{\text{R}} = -344 \text{ kJ mol}^{-1}$
- $U_{\text{R}} = -219 \text{ kJ mol}^{-1}$
- $U_{\text{R}} = 1.86 \text{ \AA}$
- $q$  to  $q_0 = -0.34$ .

## DISCUSSION

Is currently available for estimation of the complex.

we have a choice between using the Jenkins term-by-term approach, (the latter being more into account the internal structure of the advantages in that both methods, when crystal structures, require the assignment of  $n$  in order to assign a value for the lattice

Further, although the compressibility of mine the repulsion parameter  $\rho$ , compress- we have to assign a value of  $\rho$  then there pproach. The former approach offers this foreover, the latter approach, when using a potential,<sup>6</sup> requires assignment of "basic

circumvents a number of these former

ic salts, (in which form the method was y require external data to assign the charge

SHORT

CHARGE

SUM IN  
ACCUR

SOLUTION

TOTAL  
SELF E  
INTER

MODEL

MODEL

(1) (1)

(2) (1)

(3) (1)

(4) (1)

ATOM  
NA  
NA  
NA  
N  
N  
N  
O  
O  
O

CONVER

M  
0  
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17

SELF

N O

SET 1

(ii) It involves explicit minimisation of the Huggins and Mayer potential<sup>6</sup> which, from table 1, can be seen to be the obvious "next step" in the development of the theory of lattice energy calculation.

(iii) In that the approach involves a minimisation procedure, any error in assigning the repulsion parameter,  $\rho$ , (usually taken to be 0.345 Å) is compensated for by the calculation of the unknown "basic" radii of the complex ion.

(iv) Aside from choice of "basic" radii for the simpler of the ions involved in the salt, no further external data are required to assess radii.

The method of Jenkins and Waddington, the currently proposed method for cubic and non-cubic salts are compared for the halogenates,  $\text{MClO}_3$  and  $\text{MBrO}_3$  (sodium salts only) in a recent study.<sup>8</sup> The present paper illustrates the detailed application of the theory developed here for perchlorates,  $\text{MClO}_4$  ( $\text{M} = \text{Na}, \text{K}$  and  $\text{NH}_4$ ).

## THEORETICAL

We present here an extension of the theory previously developed<sup>7</sup> for cubic salts. It enables the calculation of the total lattice potential energy of salts in general and those which contain complex ions in particular. It is applicable to crystals of all symmetries, and the method tends to yield most information for salts which have low symmetry (three non-equivalent cell lengths). A general outline follows.

The total lattice energy of a salt is given by:

$$U_{\text{TOT}} = U_{\text{ELEC}} - U_{\text{R}} + U_{\text{dd}} + U_{\text{qd}} \quad (1)$$

where  $U_{\text{ELEC}}$ ,  $U_{\text{R}}$ ,  $U_{\text{dd}}$  and  $U_{\text{qd}}$  are the electrostatic, repulsion, dipole-dipole dispersion and quadrupole-dipole dispersion energies respectively. For a general salt, there exist up to three conditions (depending on the non-equivalence or otherwise of the lattice constants) of the form:

$$\left( \frac{\partial U_{\text{TOT}}}{\partial i} \right)_{i=i_0,d} = 0 \quad (2)$$

where  $i = a, b$  or  $c$ , the unit cell parameters, and the minimisation is carried out with respect to a single parameter  $i$  while retaining the other cell parameters at their equilibrium values,  $i_0$  and keeping the internal distances in the complex ion ( $= d$ ) constant.

Relationship (2) implies that:

$$\left( \frac{\partial U_{\text{R}}}{\partial i} \right)_{i=i_0,d} = \left( \frac{\partial U_{\text{ELEC}}}{\partial i} \right)_{i=i_0,d} + \left( \frac{\partial U_{\text{dd}}}{\partial i} \right)_{i=i_0,d} + \left( \frac{\partial U_{\text{qd}}}{\partial i} \right)_{i=i_0,d} \quad (3)$$

The theory develops the above relationships and uses them to determine various parameters for the salts, including "basic" radii of ions and charge distribution in complex ions.

We employ the Bertaut method,<sup>9</sup> in which the "cut-off" radius  $R$  of the charge density functions is taken as half the internal distance in the complex ions ( $= d/2$ ), to calculate the electrostatic energy and its derivatives. The choice of radius is made to ensure that it is invariant to change in lattice constant, whilst ensuring no overlap of charge density functions on the atomic centres. In this situation the total electrostatic (including self-energy of the ions) is given by:

$$U_{\text{ELEC}} = \frac{Kq}{R_K} \sum_{j=1}^N n_j q_j^2 - \frac{K}{2\pi V_K} \sum_k \sum_l \sum_i \frac{|F_{kl}|^2 \phi_{kl}^2}{S_{kl}^2} + K \sum_{r=1}^P \sum_{s=1}^P \frac{q_r q_s}{R_{rs}} \quad (4)$$

on of the Huggins and Mayer potential<sup>6</sup> which, obvious "next step" in the development of the

a minimisation procedure, any error in assigning taken to be 0.345 Å) is compensated for by the radius of the complex ion.

"radii for the simpler of the ions involved in required to assess radii.

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## THEORETICAL

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is given by:

$$E_C = U_R + U_{dd} + U_{qd} \quad (1)$$

electrostatic, repulsion, dipole-dipole dispersion energies respectively. For a general salt, there exist on the non-equivalence or otherwise of the

$$\left( \frac{\partial E}{\partial l} \right)_{l=l_0,d} = 0 \quad (2)$$

eters, and the minimisation is carried out with e retaining the other cell parameters at their e internal distances in the complex ion ( $= d$ )

$$+ \left( \frac{\partial U_{dd}}{\partial l} \right)_{l=l_0,d} + \left( \frac{\partial U_{qd}}{\partial l} \right)_{l=l_0,d} \quad (3)$$

relationships and uses them to determine various basic "radii of ions and charge distribution in

in which the "cut-off" radius  $R$  of the charge internal distance in the complex ions ( $= d/2$ ), and its derivatives. The choice of radius is made e in lattice constant, whilst ensuring no overlap mic centres. In this situation the total electro-

$$\sum_{h,k,l} \sum_{r,s} \frac{|F_{hkl}|^2 \phi_{hkl}^2}{S_{hkl}^2} + K \sum_{r=1}^p \sum_{s=1}^p \frac{q_r q_s}{R_{rs}} \quad (4)$$

where  $K = 1389.30 \text{ kJ mol}^{-1} \text{ e}^{-2} \text{ Å}$ ,  $g$  is a constant term specific to the charge density function used ( $= 25/28$  for the parabolic charge density used by us to facilitate convergence),  $\kappa$  is the number of molecules in the unit cell which has volume  $V$ ,  $n_j$  and  $q_j$  are the number of ions of the  $j$ th type bearing charge  $q_j$ .  $h, k, l$  are the indices of points on the reciprocal lattice.  $p$  is the number of atoms in the complex ion and  $R_{rs}$  is the distance between the  $r$ th and  $s$ th atoms in the same complex ion.  $|F_{hkl}|^2$  is the square of the modulus of the Coulombic structure factor,  $\phi_{hkl}$  is the square of the Fourier transform of the charge density function and  $S_{hkl}^2$  is the square of the reciprocal lattice vector.

$V$  and  $S_{hkl}^2$  are given by:

$$V = abc[1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma]^{\frac{1}{2}} \quad (5)$$

$$S_{hkl}^2 = \frac{1}{V^2} [h^2 b^2 c^2 \sin^2 \alpha + k^2 c^2 a^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma + 2hkabc^2(\cos \alpha \cos \beta - \cos \gamma) + 2kla^2 bc(\cos \beta \cos \gamma - \cos \alpha) + 2lh ab^2 c(\cos \alpha \cos \gamma - \cos \beta)] \quad (6)$$

and the derivatives with respect to lattice constants are readily obtained.

For the parabolic charge density function,<sup>10</sup> the Fourier transform  $\phi_{hkl}$  takes the mathematical form:

$$\phi_{hkl} = \left[ \frac{60(\theta \cos \theta - 3 \sin \theta + 2\theta)}{\theta^5} \right] \quad (7)$$

where

$$\theta = 2\pi R \sqrt{S_{hkl}^2} \quad (8)$$

so the derivative of  $\phi_{hkl}^2$  is obtainable once having obtained  $(\partial S_{hkl}^2 / \partial l)_{l=l_0,d}$ . Eqn (7) is similar for other charge density functions.

$|F_{hkl}|$  is given by:

$$|F_{hkl}|^2 = \left[ \sum_{r=1}^N q_r \sum_{s=1}^N \cos(\text{ARG}_{rs}) \right]^2 + \left[ \sum_{r=1}^N q_r \sum_{s=1}^N \sin(\text{ARG}_{rs}) \right]^2 \quad (9)$$

where

$$\text{ARG}_{rs} = 2\pi[hx_{rs} + ky_{rs} + lz_{rs}] \quad (10)$$

and  $x_{rs}, y_{rs}$  and  $z_{rs}$  are the fractional coordinates of  $s$ th atom of type  $r$ .

Since during the "lattice energy step" of Born-Fajans-Haber cycle, we require the complex ion to have rigid geometry we have to define the internal distances within the complex ion such that the variation of the cell lengths does not affect the internal geometry of the ion. We ensure this by incorporating  $d_a, d_b, d_c$ , the resolved components of  $d$ , the internal distance in the complex ion, parallel to the crystal axes into eqn (10) such that:

$$\text{ARG}_{rs} = 2\pi \left[ h \left( x_{rs} + \frac{d_a}{a} \right) + k \left( y_{rs} + \frac{d_b}{b} \right) + l \left( z_{rs} + \frac{d_c}{c} \right) \right] \quad (11)$$

Eqn (11) holds for terminal atoms within the complex ion while eqn (10) holds for all other atoms.

This introduces a cell length dependence into the coulombic structure factor.

$$\left( \frac{\partial |F_{hkl}|^2}{\partial l} \right)_{l=l_0,d} = 2 \left[ \sum_{r=1}^N q_r \sum_{s=1}^N \cos(\text{ARG}_{rs}) \right] \left[ \sum_{r=1}^N q_r \sum_{s=1}^N \left( \frac{2\pi m d_l}{l^2} \right) \sin(\text{ARG}_{rs}) \right] - 2 \left[ \sum_{r=1}^N q_r \sum_{s=1}^N \sin(\text{ARG}_{rs}) \right] \left[ \sum_{r=1}^N q_r \sum_{s=1}^N \left( \frac{2\pi m d_l}{l^2} \right) \cos(\text{ARG}_{rs}) \right] \quad (12)$$

where  $m = h$  for  $i = a$ ,  $m = k$  for  $i = b$ , and  $m = l$  for  $i = c$ . From eqn (4):

$$\left(\frac{\partial U_{\text{ELEC}}}{\partial i}\right) = \frac{K}{2\pi\kappa V^2} \left(\frac{\partial V}{\partial i}\right) \sum_k \sum_l \sum_i \frac{|F_{hkl}|^2 \phi_{hkl}^2}{S_{hkl}^2} - \frac{K}{2\pi\kappa V} \sum_k \sum_l \sum_i \left[ \left(\frac{\partial |F_{hkl}|^2}{\partial i}\right) \frac{\phi_{hkl}^2}{S_{hkl}^2} + \left(\frac{\partial \phi_{hkl}^2}{\partial i}\right) \frac{|F_{hkl}|^2}{S_{hkl}^2} + \left(\frac{\partial S_{hkl}^{-2}}{\partial i}\right) |F_{hkl}|^2 \phi_{hkl}^2 \right]. \quad (13)$$

Having evaluated one of the derivatives in eqn (3), we can proceed to evaluate those remaining collectively since their general dependence on the unit cell parameters is similar.

$U_R$ ,  $U_{dd}$  and  $U_{qd}$  each involve three terms derived from anion-anion, anion-cation and cation-cation interactions respectively (see calculation section). All these terms,  $T$ , are of the general form:

$$T = t \sum_j f(R_j) \quad (14)$$

where  $R_j$  is the distance of an atom from a reference atom and  $t$  is cell parameter independent. Accordingly:

$$\left(\frac{\partial T}{\partial i}\right)_{i=i_0,d} = t \sum_j \left(\frac{\partial f(R_j)}{\partial R_j}\right) \left(\frac{\partial R_j}{\partial i}\right)_{i=i_0,d} \quad (15)$$

specifically for  $U_R$ ,  $f(R_j) = \exp(-R_j/\rho)$ , for  $U_{dd}$ ,  $f(R_j) = R_j^{-6}$  and for  $U_{qd}$ ,  $f(R_j) = R_j^{-8}$ .

Remembering the considerations discussed above with regard to terminal atoms in complex ions, the derivatives in eqn (15) are readily obtained.

When complex ions are involved of the type  $YX_n^z$ , eqn (4) and (13) are expressible as parametric functions of  $q_x$ , the charge on the terminal atoms of the complex ion. The derivatives arising from eqn (15) are, in the case of  $U_R$ , sometimes expressible as a function of  $q_x$ , depending on the model chosen to represent the complex ion. In the case of  $U_{dd}$  and  $U_{qd}$ , their derivatives are not functions of  $q_x$ . Accordingly, eqn (3) takes the general form:

$$\left(\frac{\partial U_R}{\partial i}\right)_{i=i_0,d} = \sum_{\mu=0}^2 \tau_{i\mu} q_x^\mu \quad (16)$$

where

$$\tau_{i0} = C_{i0} + \left(\frac{\partial U_{dd}}{\partial i}\right)_{i=i_0,d} + \left(\frac{\partial U_{qd}}{\partial i}\right)_{i=i_0,d} \quad (17)$$

and  $C_{i0}$  is the charge independent term of  $(\partial U_{\text{ELEC}}/\partial i)_{i=i_0,d}$ .

The Huggins and Mayer potential<sup>6</sup> employed is such that no general form for  $U_R$  can easily be written which embraces all salts. The specific form for a given salt is differentiated with respect to  $i$  and equated to the right hand side of eqn (16), thereby producing up to three quadratic equations in  $\exp[\bar{r}(YX_n^z)/\rho]$  which can be solved to generate values of the "basic" radius of the complex ion as a function of  $q_x$ , the charge on the terminal atom of the complex ions. Such curves tend to intersect to form a discriminant for the determination of both  $\bar{r}(YX_n^z)$  and  $q_x$  for the salt (assuming both  $\bar{r}$  and  $\rho$  are isotropic). The assumption that the "basic" radius is isotropic is not, however, essential and as an alternative we can plot  $U_{\text{POR}}$  for a specific salt against  $q_x$ , in order to determine  $q_x$ , by substituting the radius obtained



## ENERGY MINIMISATION

$i = b$ , and  $m = 1$  for  $i = c$ . From eqn (4):

$$\frac{F_{ad}^2 \phi_{ad}^2}{S_{ad}^2} - \left( \frac{\partial^2 F_{ad}^2}{\partial i^2} \right) \frac{F_{ad}^2}{S_{ad}^2} + \left( \frac{\partial S_{ad}^2}{\partial i} \right) \frac{F_{ad}^2 \phi_{ad}^2}{S_{ad}^2} \quad (13)$$

derivatives in eqn (3), we can proceed to evaluate their general dependence on the unit cell parameters

the terms derived from anion-anion, anion-cation and cation-cation (see calculation section). All these terms,

$$= \sum_i f(R_i) \quad (14)$$

from a reference atom and  $i$  is cell parameter

$$\sum_i \left( \frac{\partial f(R_i)}{\partial R_i} \right) \left( \frac{\partial R_i}{\partial i} \right) \quad (15)$$

$R_i(\rho)$ , for  $U_{ad}, f(R_i) = R_i^{-6}$  and for  $U_{qd}, f(R_i) =$

discussed above with regard to terminal atoms eqn (15) are readily obtained.

of the type  $YX_4^+$ , eqn (4) and (13) are expressible charge on the terminal atoms of the complex ion. (5) are, in the case of  $U_{ad}$ , sometimes expressible the model chosen to represent the complex ion. derivatives are not functions of  $q_i$ . Accordingly,

$$= \sum_{i=1}^n \frac{q_i}{r_i^6} \quad (16)$$

$$\left( \frac{\partial U_{ad}}{\partial i} \right)_{i=q_0} + \left( \frac{\partial U_{qd}}{\partial i} \right)_{i=q_0} \quad (17)$$

term of  $(\partial U_{ELEC}/\partial i)_{i=q_0}$

employed is such that no general form for  $U_{ad}$  fits all salts. The specific form for a given salt and equated to the right hand side of eqn (16), quadratic equations in  $\exp [f(YX_4^+)/\rho]$  which can be "basic" radius of the complex ion as a function of  $q_i$ , the complex ions. Such curves tend to intersect termination of both  $f(YX_4^+)$  and  $q_i$  for the salt (c). The assumption that the "basic" radius is and as an alternative we can plot  $U_{TOT}$  for a determine  $q_i$ , by substituting the radius obtained

at each value of  $q_i$ , back into the Huggins and Mayer expression<sup>6</sup> to calculate  $U_R$  and hence *via* eqn (1),  $U_{TOT}$ . This point is illustrated in the results section of this paper.

When dealing with families of salts having a common gegen ion the plot of an external thermodynamic quantity related to the gaseous ion against  $q_i$  can lead to assignment of  $q_i$  and a value of the thermodynamic property and to the inclusion of all members of such a family in such a determination. This point is also illustrated in the results section.

## CALCULATIONS

For the purposes of illustrating the theory developed above we consider the perchlorate salts,  $MClO_4$  ( $M = Na, K$  or  $NH_4$ ).  $NaClO_4$  possesses the anhydrite structure,  $CaSO_4$ , with orthorhombic symmetry and space group  $Bbmm$  having ( $a_0 = 6.48 \text{ \AA}$ ,  $b_0 = 7.06 \text{ \AA}$ ,  $c_0 = 7.08 \text{ \AA}$ )<sup>11, 12</sup>  $KClO_4$  and  $NH_4ClO_4$  have the baryte,  $BaSO_4$ , structure, with orthorhombic symmetry and space group  $Pnma$  having ( $a_0 = 8.834 \text{ \AA}$ ,  $b_0 = 5.650 \text{ \AA}$ ,  $c_0 = 7.240 \text{ \AA}$ ) for  $KClO_4$ <sup>12, 13</sup> and ( $a_0 = 9.202 \text{ \AA}$ ,  $b_0 = 5.816 \text{ \AA}$ ,  $c_0 = 7.449 \text{ \AA}$ ) for  $NH_4ClO_4$ <sup>12, 14</sup>. Since all these salts possess orthorhombic symmetry, use of the *older method* of term-by-term calculation would lead to similar curves for  $\Delta H_f^\circ(ClO_4^-)(g)$  against  $q_0$  and difficulties in assigning  $q_0$ . Such a calculation would lead to three such curves. The new approach is able to assign  $q_0$  definitively and also leads to *nine* curves of  $\Delta H_f^\circ(ClO_4^-)(g)$  against  $q_0$ .

The computer program MADELUNG DERIVATIVES written in this laboratory<sup>15</sup> was used to compute  $U_{ELEC}$  and  $(\partial U_{ELEC}/\partial i)$  for  $i = a, b$  and  $c$ . These parameters are functions of  $q_0$ , the charge on the terminal atoms of the  $ClO_4^-$  ion:

$$U_{ELEC} = \sum_{\mu=0}^2 B_\mu q_0^\mu \quad (18)$$

$$\left( \frac{\partial U_{ELEC}}{\partial i} \right) = \sum_{\mu=0}^2 C_{i\mu} q_0^\mu \quad (19)$$

For the purposes of calculating  $U_{ad}$ ,  $U_{qd}$  and associated derivatives  $(\partial U_{ad}/\partial i)$  and  $(\partial U_{qd}/\partial i)$  we took the parameters  $\alpha_{Na^+} = 0.41 \text{ \AA}^3$ ,  $\alpha_{K^+} = 1.33 \text{ \AA}^3$  and  $\alpha_{NH_4^+} = 2.00 \text{ \AA}^3$  for the polarisabilities of the cations<sup>16</sup> and  $\alpha_- = 5.09 \text{ \AA}^3$  for the  $ClO_4^-$  ion (taken as equal to that of  $SO_4^{2-}$  ion in the absence of data). The characteristic energies  $\epsilon_+$  and  $\epsilon_-$  were taken for  $Na^+$   $82.55 \times 10^{12} \text{ erg molecule}^{-1}$ ,<sup>17</sup> for  $K^+$   $45.84 \times 10^{12} \text{ erg molecule}^{-1}$ ,<sup>17</sup> for  $NH_4^+$   $41.09 \times 10^{12} \text{ erg molecule}^{-1}$ <sup>18</sup> and for  $ClO_4^-$  to be  $7.6 \times 10^{12} \text{ erg molecule}^{-1}$ .<sup>19</sup> The usual approach is employed<sup>7</sup> using the equations below.

$$U_{dd} = \frac{1}{2} C_+ + \sum_{\text{ions}} R_{MM_i}^{-6} + \frac{1}{2} C_- - \sum_{\text{ions}} R_{ClCl_i}^{-6} + C_+ - \sum_{\text{ions}} R_{MCl_i}^{-6} \quad (20)$$

where

$$C_{\pm} = \frac{2e^4 Q_i Q_j}{3(\epsilon_+ + \epsilon_-)} \quad (21)$$

and

$$Q_i = \frac{3\alpha_i \epsilon_i}{2e^2} \quad (22)$$

$$U_{qd} = \frac{1}{2} D_+ + \sum_{\text{ions}} R_{MM_i}^{-8} + \frac{1}{2} D_- - \sum_{\text{ions}} R_{ClCl_i}^{-8} + D_+ - \sum_{\text{ions}} R_{MCl_i}^{-8} \quad (23)$$



where

$$D_{rs} = \frac{3C_{rs}}{2} \left[ \frac{Q_r}{p_r} + \frac{Q_s}{p_s} \right] \quad (24)$$

and  $p_r$  and  $p_s$  are the electron numbers, taken as 8 for all ions considered in this study.

For the purposes of calculating the repulsion energy,  $U_R$  and related derivatives, two models have been used for the  $\text{ClO}_4^-$  ion. The first is one which assumes a "spherical anion" to represent  $\text{ClO}_4^-$ , and in this case  $U_R$  takes the form:

$$U_R = \frac{1}{2}bc_{++} \exp\left(\frac{2\bar{r}_{M^+}}{\rho}\right) \sum_i^{\text{ions}} \exp(-R_{MM_i}/\rho) + \frac{1}{2}bc_{--} \exp\left(\frac{2\bar{r}_{\text{ClO}_4^-}}{\rho}\right) \sum_i^{\text{ions}} \exp(-R_{\text{ClCl}_i}/\rho) + bc_{+-} \exp\left(\frac{\bar{r}_{M^+} + \bar{r}_{\text{ClO}_4^-}}{\rho}\right) \sum_i^{\text{ions}} \exp(-R_{\text{MCl}_i}/\rho) \quad (25)$$

where  $\bar{r}_{M^+}$ ,  $\bar{r}_{\text{ClO}_4^-}$  are the "basic" radii of the ions and

$$c_{rs} = \left(1 + \frac{q_r + q_s}{p_r + p_s}\right); \quad (26)$$

in this case  $c_{rs}$  is independent of  $q_0$ , the charge on each oxygen atom ( $q_+ = 1, q_- = -1$ ). For the second model, which represents the  $\text{ClO}_4^-$  ion as "four spheres" centred on the oxygen atoms,  $U_R$  takes the form:

$$U_R = \frac{1}{2}bc_{++} \exp\left(\frac{2\bar{r}_{M^+}}{\rho}\right) \sum_i^{\text{ions}} \exp(-R_{MM_i}/\rho) + \frac{1}{2}bc_{--} \exp\left(\frac{2\bar{r}_0}{\rho}\right) \left[ \sum_i^{\text{ions}} \exp\left(-\frac{R_{\text{Ooi}}}{\rho}\right) - 3 \exp\left(-\frac{R_{\text{Ooiint}}}{\rho}\right) \right] + bc_{+-} \exp\left(\frac{\bar{r}_{M^+} + \bar{r}_0}{\rho}\right) \sum_i^{\text{ions}} \exp(-R_{\text{MO}_i}/\rho) \quad (27)$$

where  $\bar{r}_0$  is the "basic" radius of the oxygen atom in the  $\text{ClO}_4^-$  ion.  $R_{\text{Ooiint}}$  represents the internal O—O distances within a single  $\text{ClO}_4^-$  ion (self repulsion energy).  $c_{--}$  and  $c_{+-}$  are now linear functions of  $q_0$ .

In both models we choose a cation basic radius,  $\bar{r}_{M^+}$ , taken from ref. (20). ( $\bar{r}_{\text{Na}^+} = 0.875$ ,  $\bar{r}_{\text{K}^+} = 1.197$  and  $r_{\text{NH}_4^+} = 1.271$  Å).

Equating the derivatives of eqn (25) and (27) to the respective derivatives of the form of eqn (16) generates an equation of general parametric form:

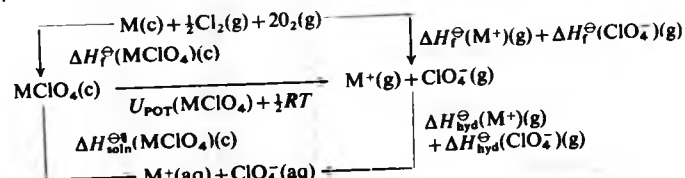
$$\theta_1 \exp\left(\frac{2\bar{r}_-}{\rho}\right) + \theta_2 \exp\left(\frac{\bar{r}_-}{\rho}\right) + \theta_3 = \sum_{\mu=0}^2 \tau_{\mu} q_0^{\mu} \quad (28)$$

where  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  include derivatives of the repulsion summations and are model dependent quantities; in the case of the second (four oxygen) model  $\theta_1$  and  $\theta_2$  are functions of  $q_0$  and  $\bar{r}_-$  represents the "basic" radius of the  $\text{ClO}_4^-$  ion or O atom, depending on the model.

The value of  $\bar{r}_-$  obtained from the solution of eqn (28) is substituted back into eqn (25) or (27) as appropriate in order to calculate  $U_R$  and hence  $U_{\text{POT}}$  as functions of  $q_0$ .

From these equations we can generate plots of  $\bar{r}_-$  against  $q_0$  and hence tentatively

assign an overall "basic" radius to the  $\text{ClO}_4^-$  ion,  $\bar{r}_{\text{ClO}_4^-}$ , using the *spherical anion* model and to the oxygen atoms in the ion,  $\bar{r}_\text{O}$ , using the *four oxygen* model. For an individual salt we can plot  $U_{\text{TOT}}$  against  $q_0$  using both models to generate values on the same plot. Finally using external thermodynamic data and the Born-Fajans-Haber cycle below we can generate plots of  $\Delta H_f^\circ(\text{ClO}_4^-)(\text{g})$  and  $\Delta H_{\text{hyd}}^\circ(\text{ClO}_4^-)(\text{g})$  against  $q_0$  since:



$$\Delta H_f^\circ(\text{ClO}_4^-)(\text{g}) = U_{\text{TOT}}(\text{MClO}_4) + \frac{1}{2}RT + \Delta H_f^\circ(\text{MClO}_4)(\text{c}) - \Delta H_f^\circ(\text{M}^+)(\text{g}) \quad (29)$$

$$\Delta H_{\text{hyd}}^\circ(\text{ClO}_4^-)(\text{g}) = \Delta H_{\text{soln}}^\circ(\text{MClO}_4)(\text{c}) - U_{\text{TOT}}(\text{MClO}_4) - \frac{1}{2}RT - \Delta H_{\text{hyd}}^\circ(\text{M}^+)(\text{g}) \quad (30)$$

for the  $\text{Na}^+$  and  $\text{K}^+$  salts and

$$\Delta H_f^\circ(\text{ClO}_4^-)(\text{g}) = U_{\text{TOT}}(\text{NH}_4\text{ClO}_4) + 2RT + \Delta H_f^\circ(\text{NH}_4\text{ClO}_4)(\text{c}) - \Delta H_f^\circ(\text{NH}_4^+)(\text{g}) \quad (31)$$

$$\Delta H_{\text{hyd}}^\circ(\text{ClO}_4^-)(\text{g}) = \Delta H_{\text{soln}}^\circ(\text{NH}_4\text{ClO}_4)(\text{c}) - U_{\text{TOT}}(\text{NH}_4\text{ClO}_4) - 2RT - \Delta H_{\text{hyd}}^\circ(\text{NH}_4^+)(\text{g}) \quad (32)$$

for  $\text{NH}_4\text{ClO}_4$ .

The literature values for the above quantities are given in table 2.

TABLE 2.—THERMODYNAMIC DATA ( $\text{kJ mol}^{-1}$ )

	$\text{NaClO}_4$	$\text{KClO}_4$	$\text{NH}_4\text{ClO}_4$	source
$\Delta H_f^\circ(\text{MClO}_4)(\text{c})$	-382.7	-430.1	-295.8	ref. (22)
$\Delta H_f^\circ(\text{M}^+)(\text{g})$	609.8	514.2	630.2	ref. (22) and (23)
$\Delta H_{\text{hyd}}^\circ(\text{M}^+)(\text{g})$	-414.6	-330.4	-332.3	ref. (24) and (23)
$\Delta H_{\text{soln}}^\circ(\text{MClO}_4)(\text{c})$	13.9	51.0	33.5	ref. (25) and (26)

## RESULTS

Table 3 gives the intermediate results obtained in the calculations.

Fig. 1 shows the plot of  $\bar{r}_{\text{ClO}_4^-}$  against  $q_0$  (from "spherical anion" model) and  $\bar{r}_\text{O}$  against  $q_0$  (from the "four oxygen" model).

Fig. 2 shows an example of a typical plot of  $U_{\text{TOT}}$  against  $q_0$  for the salt  $\text{NaClO}_4$  arising from consideration of the two models.

Finally fig. 3 shows the combined plot of  $\Delta H_f^\circ(\text{ClO}_4^-)(\text{g})$  against  $q_0$  for all the salts using the four oxygen model. The values assigned from this plot are:

$$q_0 = -0.34 \text{ proton units.} \quad (33)$$

We now compute the nine values of  $\Delta H_f^\circ(\text{ClO}_4^-)(\text{g})$  from the figure corresponding to this charge distribution and using the data in table 2 this gives, on averaging,

$$\Delta H_f^\circ(\text{ClO}_4^-)(\text{g}) = -343.7 \pm 5 \text{ kJ mol}^{-1} \quad (34)$$

TABLE 3.—RESULTS OF CALCULATIONS OF LATTICE POTENTIAL ENERGY AND  $\Delta H_f(\text{ClO}_4^- \text{Mg})$  FOR THE PERCHLORATES

	$\text{NaClO}_4$	$\text{KClO}_4$	$\text{NH}_4\text{ClO}_4$
$U_{\text{ELEC}}/\text{kJ mol}^{-1}$	$B_0$ 678.8	643.3	623.6
	$B_1$ -104.5	-30.6	-24.2
	$B_2$ -13.3	-11.1	-10.4
$(\partial U_{\text{ELEC}}/\partial a)_{b,c,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	$C_{a0}$ -56.7	-19.1	-18.3
	$C_{a1}$ -30.5	15.7	9.3
	$C_{a2}$ -12.0	4.0	2.8
$(\partial U_{\text{ELEC}}/\partial b)_{a,c,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	$C_{b0}$ -8.5	-46.4	-42.5
	$C_{b1}$ 97.7	-23.9	-13.2
	$C_{b2}$ 33.0	10.8	7.3
$(\partial U_{\text{ELEC}}/\partial c)_{a,b,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	$C_{c0}$ -35.5	-29.4	-27.9
	$C_{c1}$ -32.0	8.7	4.9
	$C_{c2}$ -20.1	-1.5	0.5
$U_{ad}/\text{kJ mol}^{-1}$	11.1	17.9	20.7
$U_{qd}/\text{kJ mol}^{-1}$	0.6	1.2	1.7
$(\partial U_{ad}/\partial a)_{b,c,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	-4.1	-3.9	-4.3
$(\partial U_{ad}/\partial b)_{a,c,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	-3.1	-6.8	-7.6
$(\partial U_{ad}/\partial c)_{a,b,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	-2.7	-4.7	-5.4
$(\partial U_{qd}/\partial a)_{b,c,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	-0.3	-0.4	-0.5
$(\partial U_{qd}/\partial b)_{a,c,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	-0.2	-0.7	-0.9
$(\partial U_{qd}/\partial c)_{a,b,d}/\text{kJ mol}^{-1} \text{\AA}^{-1}$	-0.2	-0.4	-0.6

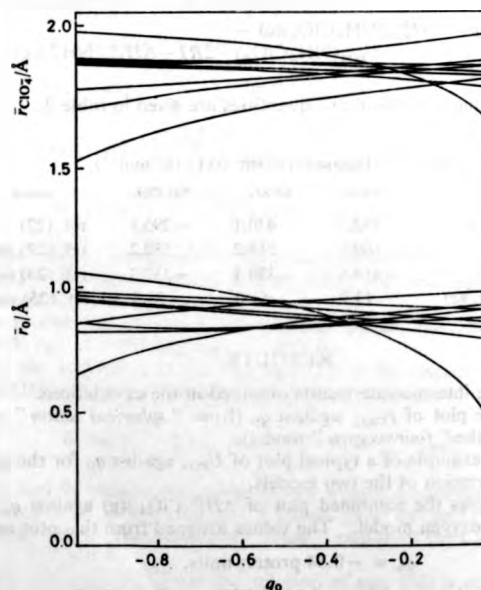
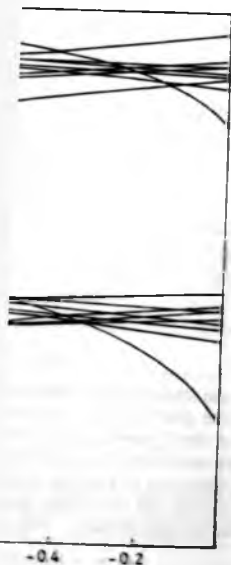


FIG. 1.—“Basic” radii,  $r(\text{ClO}_4)$  and  $r(\text{O})$  plotted as functions of  $q_0$ . [Note. If one labels curves 1-18 from the bottom of the right hand ordinate ( $q_0 = 0.0$ ) they correspond to the following sources: “four oxygen” model (1)  $\text{NaClO}_4$ ,  $i = b$ ; (2)  $\text{KClO}_4$ ,  $i = a$ ; (3)  $\text{KClO}_4$ ,  $i = c$ ; (4)  $\text{NH}_4\text{ClO}_4$ ,  $i = a$ ; (5)  $\text{NaClO}_4$ ,  $i = a$ ; (6)  $\text{NH}_4\text{ClO}_4$ ,  $i = c$ ; (7)  $\text{NaClO}_4$ ,  $i = c$ ; (8)  $\text{KClO}_4$ ,  $i = b$ ; (9)  $\text{NH}_4\text{ClO}_4$ ,  $i = b$  and “spherical anion” model (10).  $\text{NaClO}_4$ ,  $i = b$ ; (11)  $\text{KClO}_4$ ,  $i = a$ ; (12)  $\text{KClO}_4$ ,  $i = b$ ; (13)  $\text{KClO}_4$ ,  $i = c$ ; (14)  $\text{NH}_4\text{ClO}_4$ ,  $i = a$ ; (15)  $\text{NH}_4\text{ClO}_4$ ,  $i = b$ ; (16)  $\text{NH}_4\text{ClO}_4$ ,  $i = c$ ; (17)  $\text{NaClO}_4$ ,  $i = a$ ; (18)  $\text{NaClO}_4$ ,  $i = c$ ].

# MINIMISATION

LATTICE POTENTIAL ENERGY AND  $\Delta H_f(\text{ClO}_4^-)(g)$   
PER CHLORATES

	NaClO <sub>4</sub>	KClO <sub>4</sub>	NH <sub>4</sub> ClO <sub>4</sub>
0	678.8	643.3	623.6
1	-104.5	-30.6	-24.2
2	-13.3	-11.1	-10.4
a0	-56.7	-19.1	-18.3
a1	-30.5	15.7	9.3
a2	-12.0	4.0	2.8
b0	-8.5	-46.4	-42.5
b1	97.7	-23.9	-13.2
b2	33.0	10.8	7.3
c0	-35.5	-29.4	-27.9
c1	-32.0	8.7	4.9
c2	-20.1	-1.5	0.5
	11.1	17.9	20.7
	0.6	1.2	1.7
	-4.1	-3.9	-4.3
	-3.1	-6.8	-7.6
	-2.7	-4.7	-5.4
	-0.3	-0.4	-0.5
	-0.2	-0.7	-0.9
	-0.2	-0.4	-0.6



H. D. B. JENKINS AND K. F. PRATT

977

and the corresponding lattice energies are

$$U_{\text{POT}}(\text{NaClO}_4) = 643.2 \pm 2 \text{ kJ mol}^{-1} \quad (35)$$

$$U_{\text{POT}}(\text{KClO}_4) = 598.6 \pm 3 \text{ kJ mol}^{-1} \quad (36)$$

$$U_{\text{POT}}(\text{NH}_4\text{ClO}_4) = 582.5 \pm 6 \text{ kJ mol}^{-1} \quad (37)$$

where the errors quoted are standard derivatives of the values which have been averaged, and are *not* absolute errors.

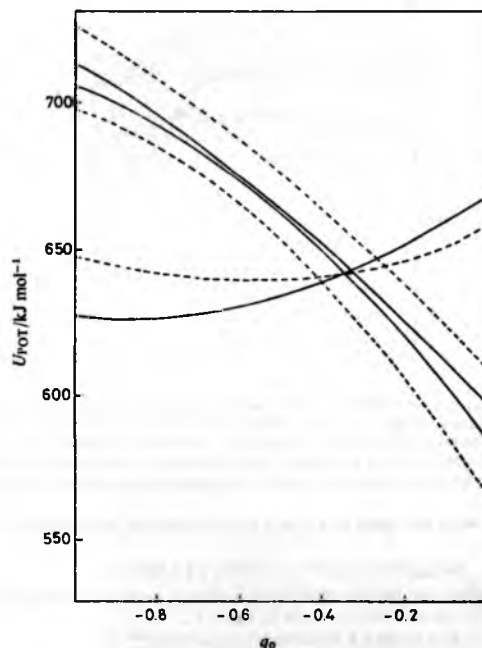


FIG. 2.—Total lattice potential energy  $U_{\text{POT}}$  for  $\text{NaClO}_4$  as a function of  $q_0$  as calculated on the two models. --- spherical anion; — four oxygen atom model. [Note. All the curves above are obtained from a single crystal structure determination for one salt. The two models give the curves shown. Assignment of  $q_0 = -0.34$  is possible using the "four oxygen" model. The corresponding value of  $U_{\text{POT}}(\text{NaClO}_4)$  is  $643 \text{ kJ mol}^{-1}$ . If we label the curves for the four oxygen model (solid) (1)–(3) from the bottom right hand ordinate ( $q_0 = 0$ ) and the spherical anion (broken) (4)–(6) the origin of the curves is as follows: (1)  $c$  derivative; (2)  $a$  derivative; (3)  $b$  derivative; (4)  $c$  derivative; (5)  $a$  derivative; (6)  $b$  derivative.]

The average "basic" radius of the  $\text{ClO}_4^-$  ion is found to be:

$$\bar{r}_{\text{ClO}_4^-} = 1.86 \pm 0.05 \text{ \AA} \quad (38)$$

and the "basic" radius for the oxygen atom in the ion is:

$$\bar{r}_o = 0.89 \pm 0.04 \text{ \AA}. \quad (39)$$

of  $q_0$ . [Note. If one labels curves 1–18 as 0.0) they correspond to the following sources: (1)  $\text{NaClO}_4$ ,  $i = a$ ; (2)  $\text{KClO}_4$ ,  $i = c$ ; (3)  $\text{NH}_4\text{ClO}_4$ ,  $i = c$ ; (4)  $\text{NaClO}_4$ ,  $i = c$ ; (5)  $\text{KClO}_4$ ,  $i = b$ ; (6)  $\text{NH}_4\text{ClO}_4$ ,  $i = b$ ; (7)  $\text{NaClO}_4$ ,  $i = c$ ; (8)  $\text{KClO}_4$ ,  $i = b$ ; (9)  $\text{NH}_4\text{ClO}_4$ ,  $i = b$ ; (10)  $\text{NaClO}_4$ ,  $i = b$ ; (11)  $\text{KClO}_4$ ,  $i = a$ ; (12)  $\text{NH}_4\text{ClO}_4$ ,  $i = a$ ; (13)  $\text{NaClO}_4$ ,  $i = b$ ; (14)  $\text{KClO}_4$ ,  $i = a$ ; (15)  $\text{NH}_4\text{ClO}_4$ ,  $i = b$ ; (16)  $\text{NaClO}_4$ ,  $i = c$ ; (17)  $\text{KClO}_4$ ,  $i = c$ ; (18)  $\text{NH}_4\text{ClO}_4$ ,  $i = c$ ].

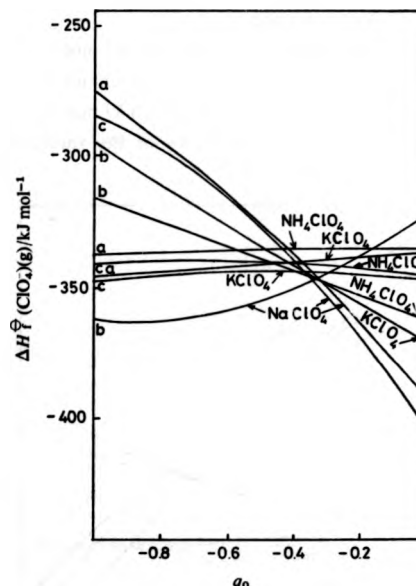


FIG. 3.— $\Delta H_f^\circ(\text{ClO}_4)(g)$  as a function of  $q_0$ . Curves are labelled according to the salt from which they originate. The letters along the ordinate indicate the derivatives from which the curves are generated. [Note. The curves for  $\text{KClO}_4$  and  $\text{NH}_4\text{ClO}_4$  generate intersection points even though the structures are very similar for the two salts. The desirability of having a third salt of differing structure is shown by the way in which the  $\text{NaClO}_4$  curves assist in fixing  $\Delta H_f^\circ(\text{ClO}_4)(g)$ .

Using eqn (29) with the data in table 2 and the charge distribution  $q_0 = -0.34$  we find:

$$\Delta H_{\text{hyd}}^\circ(\text{ClO}_4^-)(g) = -218.7 \pm 4 \text{ kJ mol}^{-1}. \quad (40)$$

We compare below the lattice energies calculated from our new approach with those which arise by use of the equations in table 1.

The Kapustinskii and simple Kapustinskii equations:<sup>33</sup>

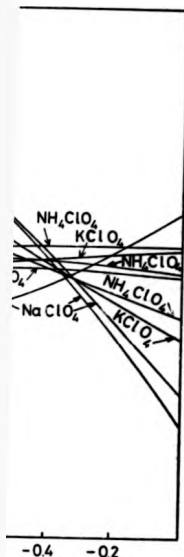
$$U_{\text{TOT}} = \frac{1214v|z_+z_-|}{(r_+ + r_-)} \left[ 1 - \frac{0.345}{(r_+ + r_-)} + 0.00870(r_+ + r_-) \right] \quad (41)$$

$$U_{\text{TOT}} = \frac{1214v|z_+z_-|}{(r_+ + r_-)} \left[ 1 - \frac{0.345}{(r_+ + r_-)} \right] \quad (42)$$

have been used in conjunction with the Goldschmidt radii of the ions ( $r_{\text{Na}^+} = 0.98 \text{ \AA}$ ,  $r_{\text{K}^+} = 1.33 \text{ \AA}$ ,  $r_{\text{NH}_4^+} = 1.43 \text{ \AA}$  and  $r_{\text{ClO}_4^-} = 2.36 \text{ \AA}$ ) with  $v = 2$  and  $|z_+z_-| = 1$ . The Born-Landé and extended Born-Landé equations:<sup>34</sup>

$$U_{\text{TOT}} = U_{\text{ELEC}} \left( 1 - \frac{1}{n} \right) \quad (43)$$

$$U_{\text{TOT}} = U_{\text{ELEC}} \left( 1 - \frac{1}{n} \right) + U_{\text{dd}} \left( 1 - \frac{6}{n} \right) + U_{\text{qd}} \left( 1 - \frac{8}{n} \right) \quad (44)$$



es are labelled according to the salt from which the derivatives from which the curves are  $\text{I}_4\text{ClO}_4$  generate intersection points even though the desirability of having a third salt of differing  $\text{ClO}_4$  curves assist in fixing  $\Delta H_f^\ominus(\text{ClO}_4)(g)$ .

and the charge distribution  $q_0 = -0.34$

$$18.7 \pm 4 \text{ kJ mol}^{-1}. \quad (40)$$

calculated from our new approach with table 1.

ii equations:<sup>33</sup>

$$\frac{45}{-r_-} + 0.00870(r_+ + r_-) \quad (41)$$

$$\frac{45}{-r_-} \quad (42)$$

Ischmidt radii of the ions ( $r_{\text{Na}^+} = 0.98 \text{ \AA}$ ,  $36 \text{ \AA}$ ) with  $v = 2$  and  $|z_+z_-| = 1$ . The ations:<sup>34</sup>

$$(43)$$

$$\left(1 - \frac{6}{n}\right) + U_{qd}\left(1 - \frac{8}{n}\right) \quad (44)$$

have been used taking the values of  $n$  given in the table 4. We take into account the distributed charge by taking  $U_{\text{ELEC}}$  in the form of eqn (18) with  $q_0 = -0.34$ . The Born-Mayer equation<sup>35</sup> and extended Born-Mayer equation (Ladd and Lee equation)<sup>36</sup>

$$U_{\text{POT}} = U_{\text{ELEC}}\left(1 - \frac{\rho}{r}\right) \quad (45)$$

$$U_{\text{POT}} = U_{\text{ELEC}}\left(1 - \frac{\rho}{r}\right) + U_{dd}\left(1 - \frac{6\rho}{r}\right) + U_{qd}\left(1 - \frac{8\rho}{r}\right) \quad (46)$$

have been used taking  $\rho = 0.345 \text{ \AA}$  and  $r$ , the nearest neighbour distance as the M-Cl distance in the lattice. Again account of the distributed charge is taken and incorporated into  $U_{\text{ELEC}}$ .

Moving across table 1 from left to right we treat the complex salt more rigorously; this is borne out in the way in which the results in table 4 agree best for the modified extended Born-Mayer equation (Ladd and Lee equation) and the present work. The Ladd and Lee equation gives normally no way of assessing  $q_0$  and it is only by substitution of the appropriate  $U_{\text{ELEC}}$  values into eqn (46) that we generate the agreement shown. The proposed method gives an assessment of the "basic" radius and charge distribution in the complex ions as well as a determination of  $\Delta H_f^\ominus(\text{ClO}_4)(g)$ .

The lattice energies derived from hydration heat and related considerations are much higher in this case than the lattice energies from other sources. This appears not to be a unique property of the perchlorates alone, and the comparison of the two approaches is the subject of continuing studies.

TABLE 4.—LATTICE ENERGIES OF PERCHLORATES

author	equation	$U_{\text{pot}}(\text{NaClO}_4)$ /kJ mol <sup>-1</sup>	$U_{\text{pot}}(\text{KClO}_4)$ /kJ mol <sup>-1</sup>	$U_{\text{pot}}(\text{NH}_4\text{ClO}_4)$ /kJ mol <sup>-1</sup>
Yatsimirskii <sup>28, 29</sup>	Kapustinakii eqn (41)*	655	611	598
Gill, Singla, Paul and Narula <sup>31</sup>	Kapustinakii eqn (42)*	643	584	569
Jenkins and Pratt	Kapustinakii eqn (41)*	673	618	603
	Kapustinakii eqn (42)*	652	596	582
	simple Born-Landé eqn (43)†	624	580	552
	(modified to take account of charge) ( $n = 8$ )	( $n = 8$ )	( $n = 9$ )	( $n = 8$ )
	simple Born-Mayer eqn (45)†	637	590	572
	(modified to take account of charge)			
	extended Born-Landé eqn (44)†	626	586	557
	(modified to take account of charge) ( $n = 8$ )	( $n = 8$ )	( $n = 9$ )	( $n = 8$ )
	extended Born-Mayer eqn (46)*†	641	598	582
	(Ladd and Lee equation)			
	(modified to take account of charge)			
Jenkins and Pratt	this work ( $q_0 = -0.34$ )*†	643	599	583
Morris <sup>32</sup>	hydration heat values	732	690	—
Saloman <sup>30</sup>	Halliwel and Nyburg equation	756	710	—

\*  $\rho = 0.345 \text{ \AA}$ ; †  $q_0 = -0.34$ .

## DISCUSSION

The advantages of the proposed method developed here for the calculation of lattice energies have been discussed in the introduction. This latest method for the calculation of lattice energies is self-contained, in that it requires no external estimates of the charge distribution in the ion.

Hojer, Heza-Hojer, de Pedrero<sup>37</sup> have recently determined  $q_0$  for  $\text{ClO}_4^-$  and find  $q_0 = -0.51$ ; Mehrota *et al.*<sup>38</sup> find  $q_0 = -0.75$ ,  $-0.67$ ,  $-0.79$  and  $-0.73$  from NDDO calculations,  $q_0 = -0.44$  from *ab initio* work and  $q_0 = -0.33$  and  $-0.64$  from CNDO calculations.



Prins<sup>39</sup> has recently calculated  $q_0 = -0.42$  for the  $\text{ClO}_4^-$  ion; earlier studies quote  $q_0 = -0.444$  (Johansen),<sup>40</sup>  $q_0 = -0.21$  (Connor, Hillier and Saunders),<sup>27</sup>  $q_0 = -0.41$ ,  $-0.39$  (Cox and Moore),<sup>41</sup>  $q_0 = -0.775$  (Best),<sup>42</sup>  $q_0 = -0.775$  (Manne),<sup>43</sup>  $q_0 = -0.814$  (Nefedov)<sup>44</sup> and  $q_0 = -0.359$  (Wagner).<sup>45</sup> Our results fit in well with the majority of these calculations.

Fig. 4 combines the two models on the same plot of  $\Delta H_f^\circ(\text{ClO}_4^-)(g)$ .

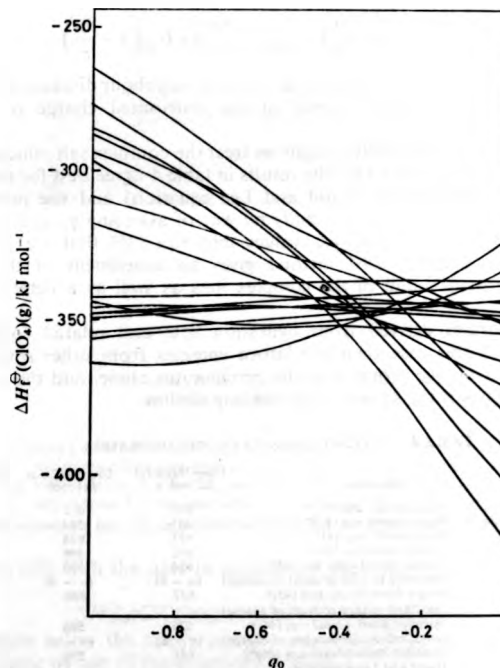


FIG. 4.— $\Delta H_f^\circ(\text{ClO}_4^-)(g)$  as a function of  $q_0$ . Both models of  $\text{ClO}_4^-$  ion. (Note. There are 18 curves which arise from two distinct models, three  $\text{MClO}_4$  salts and three different derivatives).

The standard derivatives of the basic radii are affected by anisotropy of the ions and by differing Cl—O distances in the perchlorates. In the calculations we have used the individual radii rather than the average radii specified. The standard derivations in the radii are  $<5\%$  suggesting that the degree of anisotropy in the ions of the crystals is not great.

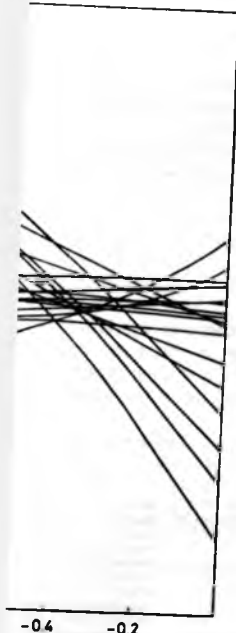
The fig. 3 based on the four oxygen atom impressively fixes  $\Delta H_f^\circ(\text{ClO}_4^-)(g)$  and the method, in that it uses minimisation conditions, is clearly superior to our other approaches.

It is not outside the scope of the present theory for it to be extended to include some estimation of the repulsion parameter  $\rho$ . Current methods (table 1) which do attempt an estimation of  $\rho$  rely on second derivatives and compressibility data. The latter data are sparse and the opportunity of generating information about  $\rho$  from

# MINIMISATION

0.42 for the  $\text{ClO}_4^-$  ion; earlier studies 0.21 (Connor, Hillier and Saunders),<sup>27</sup>  $q_0 = -0.775$  (Best),<sup>42</sup>  $q_0 = -0.775$   $r_0 = -0.359$  (Wagner).<sup>45</sup> Our results

ons.  
me plot of  $\Delta H_f^\ominus(\text{ClO}_4^-)(g)$ .



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i impressively fixes  $\Delta H_f^\ominus(\text{ClO}_4^-)(g)$  and ditions, is clearly superior to our other

theory for it to be extended to include Current methods (table 1) which do ivatives and compressibility data. The generating information about  $\rho$  from

first derivatives remains an uninvestigated yet attractive feature of the current method. The impression should not be conveyed that such a determination of  $\rho$  would be without complication.

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- <sup>1</sup> H. D. B. Jenkins and T. C. Waddington, *Chem. Phys. Letters*, 1975, **31**, 369.
- <sup>2</sup> H. D. B. Jenkins, *J.C.S. Faraday II*, 1976, **72**, 1569.
- <sup>3</sup> A. Neckel, P. Kuzmany and G. Vinek, *Z. Naturforsch.*, 1971, **26a**, 569.
- <sup>4</sup> R. C. Gearhart, J. D. Beck and R. H. Wood, *Inorg. Chem.*, 1975, **14**, 2413.
- <sup>5</sup> H. D. B. Jenkins, K. F. Pratt, B. T. Smith and T. C. Waddington, *J. Inorg. Nuclear Chem.*, 1976, **38**, 371.
- <sup>6</sup> M. L. Huggins and J. E. Mayer, *J. Chem. Phys.*, 1933, **1**, 643.
- <sup>7</sup> H. D. B. Jenkins and K. F. Pratt, *Proc. Roy. Soc. A*, 1977, **356**, 115.
- <sup>8</sup> P. Herzig, H. D. B. Jenkins and K. F. Pratt, *J. Phys. Chem. Solids*, 1978, submitted for publication.
- <sup>9</sup> E. F. Bertant, *J. Phys. Radium*, 1952, **13**, 499.
- <sup>10</sup> D. H. Templeton, *J. Chem. Phys.*, 1955, **23**, 1629.
- <sup>11</sup> K. Hermann and W. Ilge, *Z. Krist.*, 1931, **80**, 402.
- <sup>12</sup> R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 2nd edn, 1964).
- <sup>13</sup> S. Ramaseshan, K. Venkatesan and N. V. Mani, *Proc. Indian Acad. Sci. A*, 1957, **46**, 95.
- <sup>14</sup> C. S. Choi, H. J. Prask and E. Prince, *Acta Cryst. B*, 1976, **32**, 2919.
- <sup>15</sup> H. D. B. Jenkins and K. F. Pratt, *Computer Phys. Comm.*, 1978, **13**, 341.
- <sup>16</sup> J. R. Tessman, A. H. Kahn and W. Shockley, *Phys. Rev.*, 1953, **92**, 890.
- <sup>17</sup> C. E. Moore, *Atomic Energy Levels* (N.B.S. Circular 467, N.B.S., Washington D.C., U.S.A., 1958).
- <sup>18</sup> A. L. Goodliffe, H. D. B. Jenkins, S. V. Martin and T. C. Waddington, *Mol. Phys.*, 1971, **21**, 761.
- <sup>19</sup> W. H. Waggoner and M. E. Chambers, *Talanta*, 1960, **5**, 121.
- <sup>20</sup> H. D. B. Jenkins and K. F. Pratt, *Repulsion Energy and Basic Radii for Ions having Spherical Symmetry* (Res. Rept. Supp. No. 1, University of Warwick, 1976).
- <sup>21</sup> K. H. Stern, *J. Phys. Chem. Ref. Data*, 1974, **3**, 481.
- <sup>22</sup> D. R. Still and H. Prophet, *JANAF Thermochemical Tables*, 2nd edn, (NSRDS-NBS 37, 1971).
- <sup>23</sup> H. D. B. Jenkins and D. F. C. Morris, *Mol. Phys.*, 1976, **32**, 231.
- <sup>24</sup> H. D. B. Jenkins and D. F. C. Morris, *Phil. Mag.*, 1977, **35**, 1091.
- <sup>25</sup> D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, *Selected Values of Chemical Thermodynamic Properties* (N.B.S. Technical Note 270-3, U.S. Department of Commerce, U.S. Govt. Printing Office, Washington D.C., 20403, U.S.A., 1968).
- <sup>26</sup> V. B. Parker as quoted in R. C. Weast, *Handbook of Chemistry and Physics* (C.R.C. Press, Cleveland, Ohio, U.S.A., 1976, from NSRDS-NBS 2).
- <sup>27</sup> J. A. Connor, I. H. Hillier and V. R. Saunders, *Mol. Phys.*, 1972, **23**, 81.
- <sup>28</sup> K. B. Yatsimirskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1947, **411**, 453.
- <sup>29</sup> K. B. Yatsimirskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1948, **398**.
- <sup>30</sup> M. Saloman, *J. Electrochem. Soc.*, 1971, **118**, 1614.
- <sup>31</sup> D. S. Gill, J. P. S. Singla, R. C. Paul and S. P. Narula, *J.C.S. Dalton*, 1972, **522**.
- <sup>32</sup> D. F. C. Morris, *J. Inorg. Nuclear Chem.*, 1958, **6**, 295.
- <sup>33</sup> A. F. Kapustinskii, *Quart. Rev.*, 1956, **10**, 283.
- <sup>34</sup> M. Born and A. Landé, *Ber. Preuss. Akad. Wiss. (Berlin)*, 1918, **45**, 1048.
- <sup>35</sup> M. Born and J. E. Mayer, *Z. Phys.*, 1932, **75**, 1.
- <sup>36</sup> M. F. C. Ladd and W. H. Lee, *Trans. Faraday Soc.*, 1958, **54**, 34.
- <sup>37</sup> G. Hoger, S. Meza-Hoger and G. Hernandez de Pedrero, *Chem. Phys. Letters*, 1976, **37**, 301.
- <sup>38</sup> P. K. Mehrotra, J. Chandrasekhar, P. T. Manoharan and S. Subramanian, *Theor. Chim. Acta*, 1976, **41**, 257.
- <sup>39</sup> R. Prins, *J. Chem. Phys.*, 1974, **61**, 2580.
- <sup>40</sup> H. Johansen, *Theor. Chim. Acta*, 1973, **32**, 273.
- <sup>41</sup> M. M. Cox and J. W. Moore, *J. Phys. Chem.*, 1970, **74**, 627.
- <sup>42</sup> P. E. Best, *J. Chem. Phys.*, 1968, **49**, 2797.
- <sup>43</sup> R. Manne, *J. Chem. Phys.*, 1967, **46**, 4645.
- <sup>44</sup> W. Nefedov, *Phys. Stat. Solidi*, 1962, **2**, 904.
- <sup>45</sup> E. L. Wagner, *J. Chem. Phys.*, 1962, **37**, 751.

(PAPER 7/878)

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